

# **Document made available under the Patent Cooperation Treaty (PCT)**

International application number: PCT/US05/001103

International filing date: 13 January 2005 (13.01.2005)

Document type: Certified copy of priority document

Document details: Country/Office: US  
Number: 10/925,600  
Filing date: 24 August 2004 (24.08.2004)

Date of receipt at the International Bureau: 03 March 2005 (03.03.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland  
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

1286717

UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

*February 17, 2005*

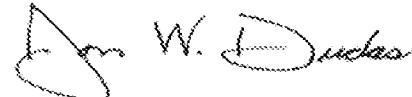
THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM  
THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK  
OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT  
APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A  
FILING DATE.

APPLICATION NUMBER: 10/925,600

FILING DATE: *August 24, 2004*

RELATED PCT APPLICATION NUMBER: PCT/US05/01103

Certified by



Under Secretary of Commerce  
for Intellectual Property  
and Director of the United States  
Patent and Trademark Office



Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

# UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.	SEN3USA
First Inventor	Arup K. SenGupta et al.
Title	METHOD OF MANUFACTURE AND USE OF HYBRID ANION . . . .
Express Mail Label No.	ED 227893744 US

**APPLICATION ELEMENTS**

See MPEP chapter 600 concerning utility patent application contents.

1.  Fee Transmittal Form (e.g., PTO/SB/17)  
*(Submit an original and a duplicate for fee processing)*
2.  Applicant claims small entity status.  
See 37 CFR 1.27.
3.  Specification [Total Pages 24]  
*(preferred arrangement set forth below)*
  - Descriptive title of the invention
  - Cross Reference to Related Applications
  - Statement Regarding Fed sponsored R & D
  - Reference to sequence listing, a table, or a computer program listing appendix
  - Background of the Invention
  - Brief Summary of the Invention
  - Brief Description of the Drawings *(if filed)*
  - Detailed Description
  - Claim(s)
  - Abstract of the Disclosure
4.  Drawing(s) (35 U.S.C. 113) [Total Sheets 19]
5. Oath or Declaration [Total Sheets 2]
  - a.  Newly executed (original or copy)
  - b.  Copy from a prior application (37 CFR 1.63(d))  
*(for continuation/divisional with Box 18 completed)*
    - i.  **DELETION OF INVENTOR(S)**  
Signed statement attached deleting inventor(s) name in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).
6.  Application Data Sheet. See 37 CFR 1.76

**ADDRESS TO:** Commissioner for Patents  
P.O. Box 1450  
Alexandria VA 22313-1450

7.  CD-ROM or CD-R in duplicate, large table or Computer Program (*Appendix*)
8. Nucleotide and/or Amino Acid Sequence Submission  
*(if applicable, all necessary)*
  - a.  Computer Readable Form (CRF)
  - b. Specification Sequence Listing on:
    - i.  CD-ROM or CD-R (2 copies); or
    - ii.  Paper
  - c.  Statements verifying identity of above copies

**ACCOMPANYING APPLICATION PARTS**

9.  Assignment Papers (cover sheet & document(s))
10.  37 CFR 3.73(b) Statement  Power of  
*(when there is an assignee)* Attorney
11.  English Translation Document (*if applicable*)
12.  Information Disclosure Statement (IDS)/PTO-1449  Copies of IDS Citations
13.  Preliminary Amendment
14.  Return Receipt Postcard (MPEP 503)  
*(Should be specifically itemized)*
15.  Certified Copy of Priority Document(s)  
*(if foreign priority is claimed)*
16.  Nonpublication Request under 35 U.S.C. 122 (b)(2)(B)(i). Applicant must attach form PTO/SB/35 or its equivalent.
17.  Other: .....

18. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in the first sentence of the specification following the title, or in an Application Data Sheet under 37 CFR 1.76:

Continuation       Divisional       Continuation-in-part (CIP)      of prior application No.: .....

Prior application information: Examiner \_\_\_\_\_ Art Unit: \_\_\_\_\_  
 For CONTINUATION OR DIVISIONAL APPS only; The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 5b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

**19. CORRESPONDENCE ADDRESS**

<input checked="" type="checkbox"/> Customer Number:	00270	<b>OR</b>	<input checked="" type="checkbox"/> Correspondence address below
Name	George A. Smith, Jr.		
Address	Box 457		
City	Spring House	State	PA
Country	USA	Telephone	215-540-9200
Name (Print/Type)	George A. Smith, Jr.	Registration No. (Attorney/Agent)	24,442
Signature			
	Date 08/24/04		

This collection of information is required by 37 CFR 1.53(b). The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

16834 U.S.PTO  
10/925600

082404

21861  
U.S. PTOApproved for use through 07/31/2006. OMB 0651-0032  
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

# FEE TRANSMITTAL for FY 2004

Effective 10/01/2003. Patent fees are subject to annual revision.

 Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT (\$ 385.00)

## Complete if Known

Application Number	
Filing Date	
First Named Inventor	Arup K. SenGupta et al.
Examiner Name	
Art Unit	
Attorney Docket No.	SEN3USA

## METHOD OF PAYMENT (check all that apply)

Check  Credit card  Money Order  Other  None

 Deposit Account:

Deposit Account Number	08-3040
Deposit Account Name	Howson and Howson

The Director is authorized to: (check all that apply)

Charge fee(s) indicated below  Credit any overpayments  
 Charge any additional fee(s) or any underpayment of fee(s)  
 Charge fee(s) indicated below, except for the filing fee to the above-identified deposit account.

## FEE CALCULATION

## 1. BASIC FILING FEE

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description	Fee Paid
1001 770	2001 385	Utility filing fee	385.00
1002 340	2002 170	Design filing fee	
1003 530	2003 265	Plant filing fee	
1004 770	2004 385	Reissue filing fee	
1005 160	2005 80	Provisional filing fee	
SUBTOTAL (1)			(\$ 385.00)

## 2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

Total Claims	Independent Claims	Multiple Dependent	Extra Claims	Fee from below	Fee Paid
19	19	-20** = 0	0	0.00	0.00
3	3	- 3** = 0	0	0.00	0.00

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description
1202 18	2202 9	Claims in excess of 20
1201 86	2201 43	Independent claims in excess of 3
1203 290	2203 145	Multiple dependent claim, if not paid
1204 86	2204 43	** Reissue independent claims over original patent
1205 18	2205 9	** Reissue claims in excess of 20 and over original patent
SUBTOTAL (2)		(\$ 0.00)

\*or number previously paid, if greater; For Reissues, see above

## 3. ADDITIONAL FEES

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description	Fee Paid
1051 130	2051 65	Surcharge - late filing fee or oath	
1052 50	2052 25	Surcharge - late provisional filing fee or cover sheet	
1053 130	1053 130	Non-English specification	
1812 2,520	1812 2,520	For filing a request for ex parte reexamination	
1804 920*	1804 920*	Requesting publication of SIR prior to Examiner action	
1805 1,840*	1805 1,840*	Requesting publication of SIR after Examiner action	
1251 110	2251 55	Extension for reply within first month	
1252 420	2252 210	Extension for reply within second month	
1253 950	2253 475	Extension for reply within third month	
1254 1,480	2254 740	Extension for reply within fourth month	
1255 2,010	2255 1,005	Extension for reply within fifth month	
1401 330	2401 165	Notice of Appeal	
1402 330	2402 165	Filing a brief in support of an appeal	
1403 290	2403 145	Request for oral hearing	
1451 1,510	1451 1,510	Petition to institute a public use proceeding	
1452 110	2452 55	Petition to revive - unavoidable	
1453 1,330	2453 665	Petition to revive - unintentional	
1501 1,330	2501 665	Utility issue fee (or reissue)	
1502 480	2502 240	Design issue fee	
1503 640	2503 320	Plant issue fee	
1460 130	1460 130	Petitions to the Commissioner	
1807 50	1807 50	Processing fee under 37 CFR 1.17(q)	
1806 180	1806 180	Submission of Information Disclosure Stmt	
8021 40	8021 40	Recording each patent assignment per property (times number of properties)	
1809 770	2809 385	Filing a submission after final rejection (37 CFR 1.129(a))	
1810 770	2810 385	For each additional invention to be examined (37 CFR 1.129(b))	
1801 770	2801 385	Request for Continued Examination (RCE)	
1802 900	1802 900	Request for expedited examination of a design application	

Other fee (specify)

\*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) (\$)

(Complete if applicable)

Name (Print/Type)	George A. Smith, Jr.	Registration No. (Attorney/Agent)	24,442	Telephone	215-540-9200
Signature				Date	08/24/04

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

This collection of information is required by 37 CFR 1.17 and 1.27. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

(SEN3USA)

METHOD OF MANUFACTURE AND USE OF HYBRID ANION EXCHANGER  
FOR SELECTIVE REMOVAL OF CONTAMINATING LIGANDS FROM FLUIDS

CROSS-REFERENCE TO RELATED APPLICATION

**[0001]** This application claims priority from provisional application 60/538,131, filed January 21, 2004.

FIELD OF THE INVENTION

**[0002]** The invention relates to the manufacture and application of hybrid anion exchangers for selective removal of contaminants from fluids.

BACKGROUND OF THE INVENTION

**[0003]** It is universally recognized that a fixed-bed sorption process is operationally simple, requires virtually no start-up time, and is forgiving toward fluctuations in feed compositions. However, in order for a fixed-bed process to be viable and economically competitive, the sorbent must exhibit high selectivity toward the target contaminant, must be durable, and must be amenable to efficient regeneration and reuse.

**[0004]** Ideally, the removal of the target contaminant should not cause major changes in pH or in the composition of the influent water. In this regard, both amorphous and crystalline Hydrated Fe Oxide (HFO) show strong sorption affinity toward both As(III) and As(V) oxyacids and oxyanions through ligand exchange in the coordination spheres of structural Fe atoms. Recent investigations using extended X-ray absorption fine structure spectroscopy (EXAFS) confirmed that As(III) and As(V) species are selectively bound to the oxide surface through formation of inner-sphere complexes. HFO particles also exhibit high sorption affinities toward phosphate, natural organic

matters, selenite and other anionic ligands. FIG. 1 shows an illustration of the binding of various solutes onto hydrated Fe(III) oxides or HFO. Commonly encountered competing ions, such as chloride or sulfate can be sorbed only through Coulombic interaction or formation of outer-sphere complexes. Thus, they exhibit poor sorption affinity toward HFO particles. In comparison, ligands such as arsenite, monovalent arsenate, divalent arsenate, phosphate, etc. are sorbed strongly through Lewis acid-base interaction or formation of inner-sphere complexes.

[0005] The traditional process of syntheses, although straightforward, produces only very fine submicron HFO particles which are unusable in fixed beds, permeable reactive barriers, or any flow-through systems, because of excessive pressure drops, poor mechanical strength and unacceptable durability. In order to overcome this problem, strong-acid cation exchangers have previously been modified to dope/disperse HFO particles for removal of arsenic. Iron-loaded cation exchange resins and alginates have also been tried for the removal of selenium and arsenic oxyanions. Although cation exchanger-loaded hydrated Fe(III) oxide (HFO) particles are capable of removing arsenates or phosphates, their removal capacities are reduced because the gel phase of the cation exchanger is negatively charged due to the presence of sulfonic acid groups. Consequently, arsenates or As(V) oxyanions and phosphates are rejected due to the Donnan co-ion exclusion effect, and dispersed HFO particles in the gel phase are not accessible to dissolved anionic ligands for selective sorption.

[0006] When macroporous cation exchangers were used as the host materials, arsenic removal capacity was not high, but on the order of 750 µg As/g of sorbent. However, when

a gel-type cation exchanger was used for dispersing HFO particles, the resulting material was ineffective altogether.

**[0007]** FIG. 2 shows a column run effluent history where a gel-type cation exchanger was loaded with eight percent HFO present as Fe. Arsenic breakthrough took place almost immediately. Thus, the material had practically no arsenic removal capacity. We have observed that HFO particles, when encapsulated within cation exchange sites as illustrated in FIG. 3, are not accessible to arsenates or other anionic ligands for selective sorption. However dispersion of HFO particles within a cation exchanger material is a relatively straightforward process.

**[0008]** Objects of the invention, therefore, are to provide a novel and more effective medium for the selective removal of arsenic species and other ligands from aqueous solutions, and to provide a method for effectively loading hydrated iron oxides onto an anion exchange resin.

#### BRIEF SUMMARY OF THE INVENTION

**[0009]** Unlike cation exchangers, anion exchangers have fixed positively charged functional groups. Thus, anionic ligands can easily permeate in and out of the gel phase without encountering the Donnan co-ion exclusion effect. If HFO particles are dispersed within a polymeric anion exchanger bead, arsenic or ligand removal capacity can be significantly increased. On the other hand, forming hydrated Fe(III) oxides within an anion exchange resin poses a major challenge due to positively charged quaternary ammonium functional groups. Consequently, heretofore, no way was known to achieve successful dispersion of HFO particles within a polymeric anion exchanger.

**[0010]** The synthesis of a selective adsorbent in accordance with the invention comprises the steps of reacting a material that exhibits anion exchange behavior with an anionic oxidant to produce an intermediate, and reacting, with the intermediate, a solution of a metal salt capable of being oxidized, thereby precipitating and dispersing a salt of the metal throughout the intermediate by the action of the oxidant, and producing an adsorbent.

**[0011]** The step of reacting the material that exhibits anion exchange behavior with an anionic oxidant is preferably carried out by passing a solution of the anionic oxidant through the material. The step of reacting a solution of a salt of a metal with the intermediate is carried out by passing a solution of the salt through the intermediate, thereby oxidizing the metal, and causing precipitation and dispersion of another salt, in which the metal is in a higher oxidation state than in the original salt. The step of reacting a solution of a metal salt with the intermediate may be followed by the step of washing the adsorbent with an organic solvent, preferably acetone, and then drying the adsorbent.

**[0012]** In preparing the adsorbent, improved results may be realized by repeating the steps of reacting a material that exhibits anion exchange behavior with an anionic oxidant, and reacting a solution of a salt of a metal with the intermediate.

**[0013]** The material that exhibits anion exchange behavior is preferably a polymeric anion exchange resin, and may comprise weak base organic ion exchange resin beads containing primary, secondary or tertiary amine groups or a mixture thereof. Alternative preferred materials are strong base organic ion exchange resin beads containing quaternary ammonium groups with a positively charged

nitrogen atom, and organic ion exchange resin beads having a polystyrene or polystyrene/divinylbenzene matrix.

**[0014]** The preferred metal salt is a solution of ferrous salt, and the preferred anionic oxidant is a permanganate, or a hypochlorite.

**[0015]** The adsorbent thus produced comprises a polymeric anion exchange resin containing dispersed particles of an oxygen-containing compound of iron, and is capable of selective removal of ligands from a fluid stream brought into contact with the adsorbent. The adsorbent is especially effective in removing ligands such as arsenates, arsenites, chromates, molybdates, selenites, and vanadates from a stream of drinking water, groundwater, industrial process water or industrial effluent.

**[0016]** In a preferred embodiment, an adsorbent bed for the selective removal of ligands from the aqueous solution is prepared by passing a solution containing an oxidizing anion such as a permanganate, persulfate or hypochlorite, through a bed of polymeric anion exchange resin. Thereafter a solution of a ferrous salt, such as ferrous sulfate, is passed through the bed, thereby simultaneously desorbing the oxidizing anion and oxidizing the ferrous ion to a ferric ion. This causes precipitation, and uniform dispersion, of a solid, hydrated ferric oxide, within the polymeric anion exchange resin. Anionic ligands such as arsenates, chromates, oxalates, phosphates, phthalates, etc., can permeate in and out of the gel phase and are not subjected to the Donnan exclusion effect. Consequently, anion exchanger-supported HFO micro particles exhibit significantly greater capacity, in comparison with cation exchanger-supported particles, for removal of arsenates, arsenites, and other arsenic oxyanions, as well as other ligands.

**[0017]** Another advantage of the invention is that the physical properties of the anion exchange material can supply structural integrity to materials that are otherwise friable and weak. Thus, by dispersion of HFO particles into anion exchange materials, it is possible to synthesize a bed that exhibits superior materials properties when compared to HFO particles that, by themselves are subject to granulation and agglomeration. The improved physical robustness afforded by the use of an anion exchange material allows for use of HFO particles under more demanding conditions such as higher pressures, increased flow, etc. The improved physical robustness of the hybrid material also allows for effective regeneration and reuse of the bed, and reduces the need for backwashing and other maintenance measures common in the treatment of streams with hydrous metal oxides that are not supported by substrates.

**[0018]** Other objects, details and advantages of the invention will be apparent from the following detailed description when read in conjunction with the drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0019]** FIG. 1 is a schematic diagram illustrating the binding of various solutes onto hydrated Fe(III) oxides;

**[0020]** FIG. 2 is a graph of the effluent history for arsenic during a column run using a hybrid cation exchanger gel;

**[0021]** FIG. 3 is a schematic diagram illustrating why an HFO doped cation exchange resin is unable to offer significant arsenic sorption capacity;

**[0022]** FIG. 4(a) and 4(b) are schematic diagrams illustrating first and second steps in the preparation of a hybrid anion exchanger sorbent;

**[0023]** FIGs. 5(a), 5(b) and 5(c) are respectively a photograph of macroporous, hybrid anion exchange sorbent particles, a scanning electron microphotograph of a sliced parent polymer bead, and a scanning electron microphotograph of a sliced hybrid anion exchange bead;

**[0024]** FIG. 6 is a schematic diagram of a set-up for fixed bed column runs and regeneration tests;

**[0025]** FIG. 7(a) is a graph showing the effluent histories for sulfate and arsenic during a column run with a parent anion exchanger in chloride form, showing early arsenic break-through;

**[0026]** FIG. 7(b) is a graph of the effluent history for arsenic during a column run using a macroporous hybrid cation exchanger;

**[0027]** FIG. 7(c) is a graph of the effluent history for arsenic during a column run using a macroporous hybrid anion exchanger;

**[0028]** FIG. 8 is a graph comparing the effluent histories for arsenic in a hybrid gel-type cation exchanger and a hybrid gel-type anion exchanger;

**[0029]** FIG. 9 is a graph comparing As(V) and silica breakthrough profiles during the treatment for groundwater using a freshly prepared, macroporous, hybrid anion exchanger;

**[0030]** FIG. 10 is a graph illustrating the arsenic concentration profile during typical regeneration of a hybrid anion exchange resin;

**[0031]** FIG. 11 is a graph of the effluent histories of As(V) and Cr(VI) during a column run using a macroporous hybrid anion exchanger;

**[0032]** FIG. 12 is a graph showing the concentration profiles of arsenic and chromium during regeneration of a macroporous hybrid anion exchanger;

**[0033]** FIG. 13 is a graph showing breakthrough profiles for phosphorous and other anions during a column run using a macroporous hybrid anion exchanger;

**[0034]** FIG. 14 is a graph showing the effluent histories for arsenic during two consecutive column runs using a macroporous hybrid anion exchanger with the same contaminated groundwater feed;

**[0035]** FIG. 15 is a graph showing the concentration of iron in the effluent during a column run using macroporous hybrid anion exchanger particles

**[0036]** FIGS. 16(a) and 16(b) are x-ray diffractograms of freshly prepared, and used, hybrid anion exchange particles, respectively;

**[0037]** FIG. 17 is a graph showing a comparison of vanadate effluent histories for a hybrid anion exchanger and a parent anion exchanger; and

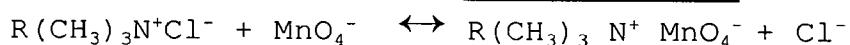
**[0038]** FIG. 18 is a graph showing a comparison of molybdate effluent histories for a hybrid anion exchanger and a parent anion exchanger.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0039]** Since  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  are cations, they are repelled by an anion exchanger's positively charged functional groups and cannot be loaded onto anion exchange resins. Thus, the technique, used previously for dispersing HFO particles within cation exchanger beads, is not applicable when anion exchanger beads serve as the host materials. We have discovered, however, that HFO particles can be

supported in anion exchanger by a series of steps, a preferred example of which is as follows.

[0040] As a first step, Permanganate anion ( $MnO_4^-$ ) is loaded onto an anion exchange resin (for example A-500P, an anion exchange resin with quaternary ammonium functional groups in chloride form, available from The Purolite Company of Bala Cynwyd, Pennsylvania). The loading of the resin with permanganate anion is carried out by passing potassium permanganate solution (500 mg/L  $KMnO_4$ ) through the bed. This may be carried out, for example by passing a 500 mg/L  $KMnO_4$  solution through the bed to achieve the following reaction:

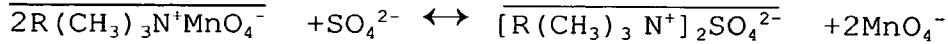


$\overline{R(CH_3)_3N^+Cl^-}$  is an anion exchange resin with a quaternary ammonium functional group in chloride form.

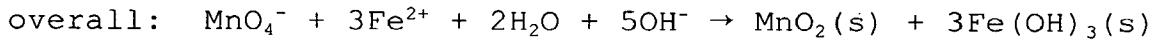
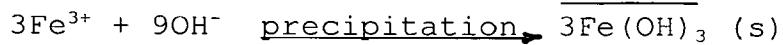
[0041] Anion exchange resins from other manufacturers may of course be used. Particles sizes of the anion exchange resins are preferably in the range from 300  $\mu\text{m}$  to 1000  $\mu\text{m}$ .

[0042] The second step is concurrent permanganate desorption, Fe(II) oxidation and HFO formation within the anion exchanger. During this step, the permanganate loaded anion exchanger is brought into contact with 5% ferrous sulfate solution. Desorption of  $MnO_4^-$  by sulfate, reduction of  $MnO_4^-$  to  $MnO_2(s)$  and oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  and finally, precipitation of  $Fe(OH)_3(s)$  within the anion exchanger beads, took place in accordance with the following:

$MnO_4^-$  desorption:



Fe(II) oxidation and formation of Ferric Hydroxide:



(The overbars and (s) denote solid phase.)

**[0043]** The third step is an acetone wash and drying. Anion exchanger beads from the second step are washed with acetone and dried in a furnace at 35°C for twelve hours.

**[0044]** The major steps of the process, that is, the first and second steps, are depicted in FIGS. 4A and 4B. These steps can be repeated to achieve greater Fe(III) loading. Also, the manganese content within the anion exchanger decreases with multiple cycles, and this is a desirable phenomenon from an application viewpoint. During the third step, the use of acetone reduced the dielectric constant of the water and enhanced the agglomeration of HFO submicron particles through suppression of surface charges. HFO agglomerates were irreversibly encapsulated within the spherical anion exchanger beads. Turbulence and mechanical stirring do not result in any noticeable loss of HFO particles.

**[0045]** Both gel and macroporous anion exchanger beads (Purolite A-400 and A-500P) were used in our study. Mass loading of HFO onto the anion exchanger varied from 10-15% as Fe; the manganese content was less than 1% by mass as

Mn. FIG. 5A shows Hybrid Anion Exchanger (HAIX) particles. FIG. 5B is a scanning electron microphotograph (SEM) of a sliced parent polymer bead, in which the presence of macropores can be readily observed. FIG. 5C shows a sliced HAIX particle containing HFO nanoparticles.

**[0046]** While the polymeric anion exchanger beads exhibit excellent hydraulic properties and durability during fixed-bed column runs, the dispersed HFO microparticles serve as active sorbents for target ligands.

**[0047]** By way of example, details of the steps carried out in a typical laboratory synthesis of hybrid anion exchanger particles are as follows.

**[0048]** In a 4.0 liter container filled with 500 mg/L solution of potassium permanganate, 30 g of Purolite anion exchanger resin were immersed the solution for 30 minutes with intermittent stirring. The resin loaded with permanganate was rinsed twice with deionized water. Thereafter, the permanganate-loaded resin was immersed in 1.0 liter of 5.0% (w/v) ferrous sulfate solution and shaken for four hours. The modified resin (hybrid anion exchanger) was then rinsed several times with deionized water. These steps were repeated for a second and third cycle of iron loading. Following each cycle, a sample of about 50 mg of the hybrid anion exchanger was taken for iron and manganese content analysis.

**[0049]** The hybrid resin was rinsed with deionized water and acetone, and then dried in an oven at 35° C for 12 hours. Both macroporous and gel-type anion exchangers from The Purolite Company, namely, Purolite A-500P and A-400, were used as the parent materials. The iron and manganese loading of HAIX particles were found by digesting twice with 10% sulfuric acid for 24 hours at room temperature.

The iron and manganese values at the end of each cycle of preparation were as follows:

For HAIX-M (Macroporous parent resin)

Cycle	Iron content* (mg/g of hybrid anion exchanger)	Manganese content* (mg/g of hybrid anion exchanger)
1	57.3	31.3
2	130.1	5.0
3	162.0	1.2

For HAIX-G (Gel parent resin)

Cycle	Iron content* (mg/g of hybrid anion exchanger)	Manganese content* (mg/g of hybrid anion exchanger)
1	35.0	4.5
2	52.2	0.8
3	60.0	0.2

\* Based on dried hybrid anion exchanger beads

**[0050]** Approximately ten different batches of HAIX-M and five different batches of HAIX-G have been synthesized. The iron content for HAIX-M after three cycles varied between 120-175 mg Fe/g, while the iron content for HAIX-G was between 70-100 mg Fe/g.

**[0051]** It was observed that the white color of the macroporous anion exchange resin changed to purple during loading with permanganate ( $MnO_4^-$ ) ion. Following the addition of ferrous sulfate solution, the purple color of the resin gradually changed to light brown. A uniform light brown color characterizes the completion of hydrated ferric oxide or HFO formation within the resin beads. Approximately four hours are needed for this step to be completed.

**[0052]** Laboratory tests were conducted to prepare HAIX using sodium hypochlorite (NaOCl) solution following the same experimental protocol. By way of example, details of the steps carried out in laboratory synthesis of hybrid anion exchanger particles using hypochlorite ions ( $OCl^-$ ) are as follow.

**[0053]** In a 4.0 liter container filled with 500 mg/L of NaOCl solution, 30 g of macroporous anion exchanger resin were immersed into the NaOCl solution for 30 min with intermittent stirring. The resin loaded with hypochlorite anion was then rinsed twice with deionized water. The hypochlorite-loaded resin was then immersed in 1.0 L of 5.0% (w/v) ferrous sulfate solution and shaken for four hours. The modified resin (hybrid anion exchanger) was then rinsed several times with deionized water.

**[0054]** The above steps were repeated for a second and third cycle of iron loading. Following each cycle, a sample of about 50 mg of the hybrid anion exchanger was taken for iron content analysis.

**[0055]** The hybrid resin was rinsed with deionized water and acetone, and then dried in an oven at 35°C for 12 hours. The iron loading was found to be as follows:

Cycle	Iron Content* (mg/g of hybrid anion exchanger)
1	10.0
2	25.0
3	40.0

\* Based on dried hybrid anion exchanger beads.

**[0056]** Since the iron loading was significantly less with hypochlorite than with permanganate, the performance evaluation of HAIIX during fixed-bed column runs and other sorption studies were carried out on products obtained using permanganate as oxidizing agent.

**[0057]** In the evaluation of the performance of HAIIX the following experimental protocol was used.

**[0058]** A series of fixed-bed experiments were carried out to evaluate the As(III) and As(V) removal capacities of HAIIX. The experimental set-up is illustrated in FIG. 6, where contaminated water from a reservoir 20 was pumped by a pump 22 into a column 24 containing HAIIX beads 26 over a glass fiber layer 28. Regenerant in reservoir 30 was pumped into the column by pump 32. The effluent was collected in effluent sample tubes 34.

**[0059]** Using this test set-up, tests were also conducted to validate the ability of HAIIX to remove chromate, phosphate and natural organic matter. The following results are noteworthy:

**[0060]** FIGs. 7A - 7C provide As(III) effluent histories for three separate column runs under nearly identical conditions using respectively Parent Anion Exchanger Purolite A-500P in chloride form in FIG. 7A, HFO loaded macroporous cation exchanger in FIG. 7B, and Hybrid Anion

Exchanger or HAIIX in FIG. 7C. The abscissa (C/Co) represents the fraction of the influent concentration present at the exit of the column.

**[0061]** As shown in FIG. 7A, the parent anion exchanger was unable to remove As(III). The empty bed contact time (EBCT) was 4.5 minutes. The influent solution contained 100 µg/L As(III), 170 mg/L SO<sub>4</sub><sup>2-</sup>, 90 mg/L Cl<sup>-</sup>, 100 mg/L HCO<sub>3</sub><sup>-</sup>, and had a pH of 6.2. Arsenic broke through immediately, and long before the sulfate breakthrough.

**[0062]** As shown in FIG. 7B, the HFO loaded cation exchanger removed As(III) over more than 2000 bed volumes, with a breakthrough concentration of 10 µg/L at about 2500 bed volumes. In this case, the EBCT was 3.1 minutes. The influent solution contained 100 µg/L As(III), 122 mg/L SO<sub>4</sub><sup>2-</sup>, 70 mg/L Cl<sup>-</sup>, 100 mg/L HCO<sub>3</sub><sup>-</sup>, and had a pH of 7.2.

**[0063]** In the experiment depicted in FIG. 7C, the experimental parameters were the same as in FIG. 7A. That is, the EBCT was 4.5 minutes, and the influent solution contained 100 µg/L As(III), 170 mg/L SO<sub>4</sub><sup>2-</sup>, 90 mg/L Cl<sup>-</sup>, 100 mg/L HCO<sub>3</sub><sup>-</sup>, and had a pH of 6.2., As illustrated in FIG. 7C, the HAIIX, or HFO loaded anion exchanger, treated nearly 12,000 bed volumes of contaminated feed water before the arsenic concentration in the effluent reached 10 µg/L. The HAIIX-M (Macroporous hybrid anion exchanger offered a six-fold greater As(III) removal capacity over the HCIX-M (Macroporous hybrid cation exchanger).

**[0064]** To validate the hypothesis that the Donnan Co-ion exclusion effect in the host material significantly influences the arsenic removal capacity of hydrated iron oxide particles, one gel-type cation exchanger (HCIX-G, using Purolite C-100) and one gel-type anion exchanger (HAIIX-G, using Purolite A-400) were loaded with iron oxide particles. Subsequently two column runs were carried out

separately for arsenic removal, using these two materials. The Fe content of the HAIX-G was 60 mg/g of HAIX-G, and the Fe content of the HCIX-G was 70 mg/g of HCIX-G. The tests were carried out under identical experimental conditions. The superficial liquid velocity (SLV) was 0.60 m/h, and the EBCT was 3.9 minutes. The influent contained 100  $\mu\text{g/L}$  As(V), 120 mg/L  $\text{SO}_4^{2-}$ , 100 mg/L  $\text{Cl}^-$ , 100 mg/L  $\text{HCO}_3^-$ , and had a pH of 7.3

**[0065]** FIG. 8 shows the arsenic effluent histories for the two column runs. The hybrid cation exchanger offered practically no arsenic removal, even with a slightly higher iron content; the hybrid anion exchanger, or HAIX, on the contrary removed arsenic at well over 10,000 bed volumes, all other conditions being identical.

**[0066]** The groundwater in Albuquerque, New Mexico is contaminated with arsenic, and also contains a high level of dissolved silica. About twenty gallons of contaminated groundwater were collected from Albuquerque, and a column run was carried out using macroporous HAIX. The SLV was 0.83 m/h and the EBCT was 3.8 minutes. The influent contained 4.6  $\mu\text{g/L}$  As(V), 33 mg/L of silica and 0.46 mg/L of phosphorus. The pH of the influent was 7.6.

**[0067]** FIG. 9 shows the effluent history for arsenic removal. Even with 33 mg/L of dissolved silica present in the contaminated water, arsenic removal was very good. Arsenic breakthrough of 10 parts per billion was observed after 7,200 bed volumes, while silica broke through from the column within 500 bed volumes.

**[0068]** An Arsenic loaded HAIX-M column can be very efficiently regenerated using a solution of 3% NaCl and 2% NaOH at a pH of 12.4 and with an EBCT of 5.6 minutes. As shown in FIG. 10, over 90% of the arsenic was desorbed within 10 bed volumes.

**[0069]** Arsenate and Chromate can be removed simultaneously, as illustrated in FIG. 11, which illustrates the effluent histories of AS(V) and Cr(VI) during a column run with a macroporous hybrid anion exchanger (HAIX-M). Here the EBCT was 3.8 minutes. The influent was a representative feedwater containing 100 µg/L As(V), 100 µg/L Cr(VI), 120 mg/L SO<sub>4</sub><sup>2-</sup>, 125 mg/L Cl<sup>-</sup>, and 100 mg/L HCO<sub>3</sub><sup>-</sup>, and had a pH of 7.1. The HAIX column was fed with the representative synthetic feed water. The HAIX column was shown to be very effective in removing both Arsenic(V) and Chromium(VI) simultaneously up to nearly 2000 bed volumes.

**[0070]** Upon exhaustion, the column was regenerated using 2% NaOH and 3% NaCl. FIG. 12 shows the concentration profiles of arsenic and chromium during regeneration of the HAIX-M at an EBCT of 3.9. The desorption of arsenate and chromate was shown to be very efficient.

**[0071]** FIG. 13 illustrates the removal of phosphate using the hybrid anion exchanger. A HAIX column was fed with a feed solution containing phosphate along with other commonly encountered anions. Specifically the influent contained 4.43 mg/L phosphate (as P), 90 mg/L Cl<sup>-</sup>, 42 mg/L SO<sub>4</sub><sup>2-</sup>, 56 mg/L NO<sub>3</sub><sup>-</sup>, and 78 mg/L HCO<sub>3</sub><sup>1</sup>, and had a pH of 7.1. the EBCT was 3.3 minutes. The effluent history for P, as depicted in FIG. 13, confirms the ability of HAIX to remove phosphate selectively in the presence of other competing anions, namely, chloride and sulfate.

**[0072]** One HAIX column was run for three successive cycles. After each cycle, the column was regenerated with 2% NaOH and 3% NaCl. FIG. 14 shows the effluent histories for arsenic in two successive column runs using groundwater collected from a contaminated site in Ontario, Canada. The SLV was 1.58 m/h and the EBCT was 1.56 minutes. The

influent contained 430 µg/L As, 280 µg/L P, 3.0 mg/L TOC, 11.9 mg/L SO<sub>4</sub><sup>2-</sup>, 6.4 mg/L Cl<sup>-</sup>, 21.9 mg/L NO<sub>3</sub><sup>-</sup>, and had a pH of 7.2. The arsenic effluent histories remained essentially the same. These results provide evidence that HAIX can be regenerated and reused for multiple cycles without a significant loss in arsenic removal capacity.

**[0073]** FIG. 15 shows the concentration of total iron released during a lengthy column run under conditions in which the SLV was 0.70 m/h and the EBCT was 4.5 minutes. The influent contained 100 µg/L As(III), 170 mg/L SO<sub>4</sub><sup>2-</sup>, 90 mg/L Cl<sup>-</sup>, 100 mg/L HCO<sub>3</sub><sup>-</sup>, and had a pH of 6.2. The iron concentration at the exit of the column was quite low (less than 3 µg/L) for nearly 15,000 bed volumes. The loss of iron from HAIX is negligible (30 µg/g HAIX-M) compared to its total capacity (120-150 mg Fe/g HAIX).

**[0074]** It is plausible that, with aging and continued usage, amorphous HFO particles could gradually become more crystalline leading to the formation of goethite, hematite, etc. However, FIGs. 16A and 16B show a comparison of X-ray diffraction (XRD) patterns of freshly prepared (FIG. 16A) versus used (FIG. 16B) HAIX samples. Both patterns are quite similar, with very minor changes. It is unlikely that HFO nanoparticles embedded in the anion exchanger underwent any structural changes.

**[0075]** FIG. 17 illustrates the performance of a hybrid anion exchanger in accordance with the invention in removing Vanadate from tap water spiked with 3 mg/L Vanadate as V. Two effluent histories are shown, one for the parent anion exchanger, and the other for the hybrid anion exchange material. As shown by the graph, the vanadate almost immediately began to pass through the parent anion exchanger, whereas, in the case of the hybrid anion exchange material, measurable amounts of vanadate

began to be detected only after about 3000 bed volumes, and remained at a level below 200 parts per billion at 8000 bed volumes.

**[0076]** Performance of the hybrid anion exchanger in accordance with the invention in the removal of molybdates was also effective as shown by FIG. 18. Two column runs were carried out, one using the parent anion exchanger and the other using the hybrid anion exchanger, on an influent consisting of tap water spiked with 3 mg/L of Molybdate as Mo. With the parent anion exchanger, Molybdate began to break through at about 100 bed volumes, and rose from a level of about 100 µg/L at about 300 bed volumes to about 1700 µg/L at 1300 bed volumes. On the other hand, in the case of the hybrid anion exchanger, Molybdate remained at a level below 100 µg/L up to about 1000 bed volumes and rose only to about 400 µg/L at 1300 bed volumes.

**[0077]** Numerous modifications can be made to the invention as described. As indicated previously, any of a wide variety of anion exchange resins can be used to carry out the selective removal of ligands. For example, as alternatives to strong base anion exchange resins having quaternary ammonium functional groups with a positively charged nitrogen atom, other anion exchange materials can be used, such as weak base organic ion exchange resin beads containing primary, secondary or tertiary amine groups or a mixture thereof; organic ion exchange resin beads having a polystyrene or polystyrene/divinylbenzene matrix; organic ion exchange resin beads having a polyacrylic matrix; organic or inorganic membranes; and polymeric fiber or fibrous anion exchange materials.

**[0078]** In principle, any anionic oxidizing agent can be used in place of permanganate. For example, in addition to hypochlorite, mentioned previously, other anionic oxidants,

for example persulfates, bromates and iodates, may be used. The intermediate, produced by reacting the anion exchange material with an anionic oxidant, may be reacted with a solution of an oxidizable salt of a metal, preferably a ferrous salt such as ferrous sulfate, ferrous ammonium sulfate, ferrous chloride or ferrous acetate. The hydrated iron oxide particles precipitated in the anion exchange material can take various forms, such as hematite, geothite, magnetite and ferrihydrite.

**[0079]** Still other modifications may be made to the apparatus and method described above without departing from the scope of the invention as defined in the following claims.

CLAIMS

1. A method for synthesizing a selective adsorbent comprises the steps of:

reacting a material that exhibits anion exchange behavior with an anionic oxidant to produce an intermediate; and  
reacting, with said intermediate, a solution of a salt of a metal, said salt being capable of being oxidized, thereby precipitating and dispersing a salt of said metal throughout the intermediate by the action of the oxidant and producing an adsorbent.

2. A method according to claim 1, in which the step of reacting said material that exhibits anion exchange behavior with an anionic oxidant is carried out by passing a solution of said anionic oxidant through said material, and in which the step of reacting a solution of a salt of a metal with said intermediate is carried out by passing a solution of said salt through said intermediate.

3. A method according to claim 1, in which the step of reacting a solution of a salt of a metal with said intermediate is followed by the step of washing the adsorbent with an organic solvent.

4. A method according to claim 1, in which the step of reacting a solution of a salt of a metal with said intermediate is followed by the step of washing the adsorbent with acetone.

5. A method according to claim 1, in which the step of reacting a solution of a salt of a metal with said

intermediate is followed by the steps of washing and drying the adsorbent.

6. A method according to claim 1 in which, in preparing said selective adsorbent, said steps of reacting a material that exhibits anion exchange behavior with an anionic oxidant, and reacting a solution of a salt of a metal with said intermediate, are repeated.

7. The method according to claim 1, in which said material that exhibits anion exchange behavior is a polymeric anion exchange resin.

8. The method according to claim 1, in which said material that exhibits anion exchange behavior comprises weak base organic ion exchange resin beads containing primary, secondary or tertiary amine groups or a mixture thereof.

9. The method according to claim 1, in which said material that exhibits anion exchange behavior comprises strong base organic ion exchange resin beads containing quaternary ammonium groups with a positively charged nitrogen atom.

10. The method according to claim 1, in which said material that exhibits anion exchange behavior comprises organic ion exchange resin beads having a polystyrene or polystyrene/divinylbenzene matrix.

11. The method according to claim 1, in which the precipitated and dispersed salt of said metal is an oxygen-containing compound of iron.

12. The method according to claim 1, in which the solution of a salt of a metal is a solution of ferrous salt.

13. The method according to claim 1, in which said anionic oxidant is a permanganate.

14. The method according to claim 1, in which said anionic oxidant is a hypochlorite.

15. An adsorbent for the selective removal of ligands from fluids, said adsorbent comprising a polymeric anion exchange resin containing dispersed particles of an oxygen-containing compound of iron.

16. A method of removing contaminants from a fluid stream, wherein said fluid stream is brought into contact with an adsorbent comprising an HFO-impregnated anion exchange material.

17. The method according to claim 16, in which said contaminants are ligands.

18. The method according to claim 16, in which said contaminants are ligands containing one or more anions from the group consisting of arsenates, arsenites, chromates, molybdates, selenites, and vanadates.

19. The method according to claim 16, in which said fluid stream is a stream of drinking water, groundwater, industrial process water or industrial effluent.

#### ABSTRACT OF THE DISCLOSURE

Polymeric anion exchangers are used as host materials in which hydrated Fe(III) Oxides (HFO) are irreversibly dispersed within the exchanger beads. Since the anion exchangers have positively charged quaternary ammonium functional groups, anionic ligands such as arsenates, chromates, oxalates, phosphates, phthalates can permeate in and out of the gel phase and are not subjected to the Donnan exclusion effect. Consequently, anion exchanger-supported HFO micro particles exhibit significantly greater capacity to remove arsenic and other ligands in comparison with cation exchanger supports. Loading of HFO particles is carried out by preliminary loading of the anion exchange resin with an oxidizing anion such as  $\text{MnO}_4^-$  or  $\text{OCl}^-$ , followed by passage of a Ferrous Sulfate solution through the resin.

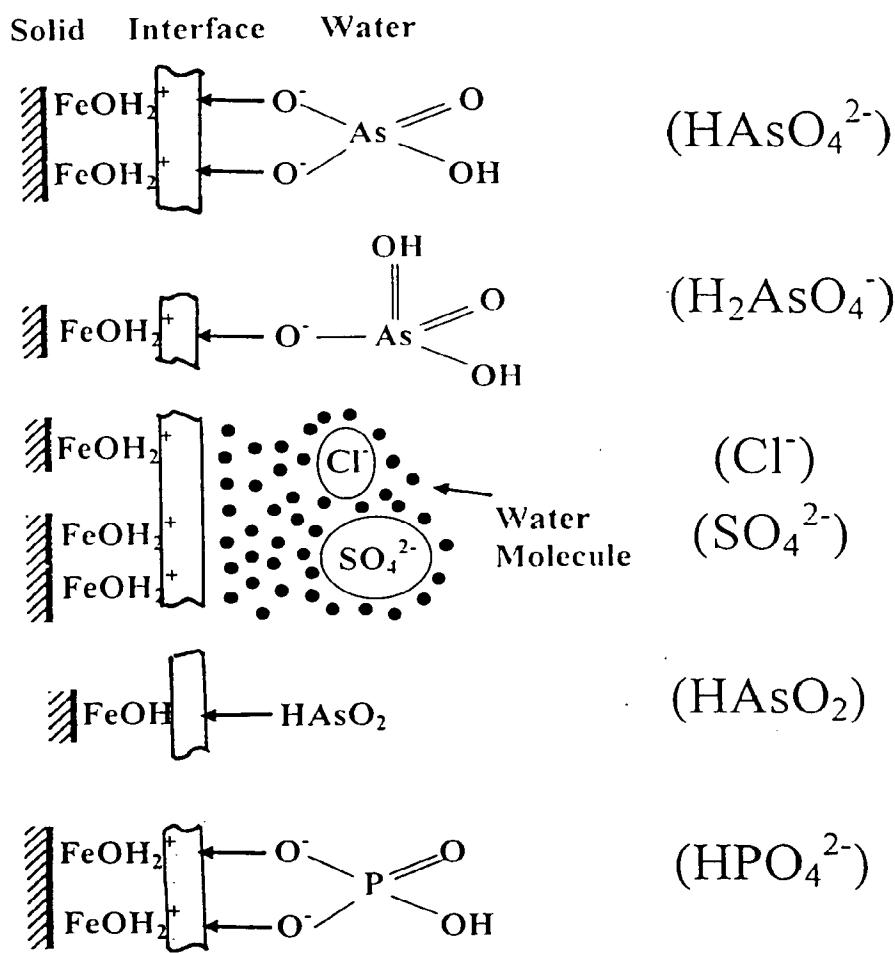


FIG. 1

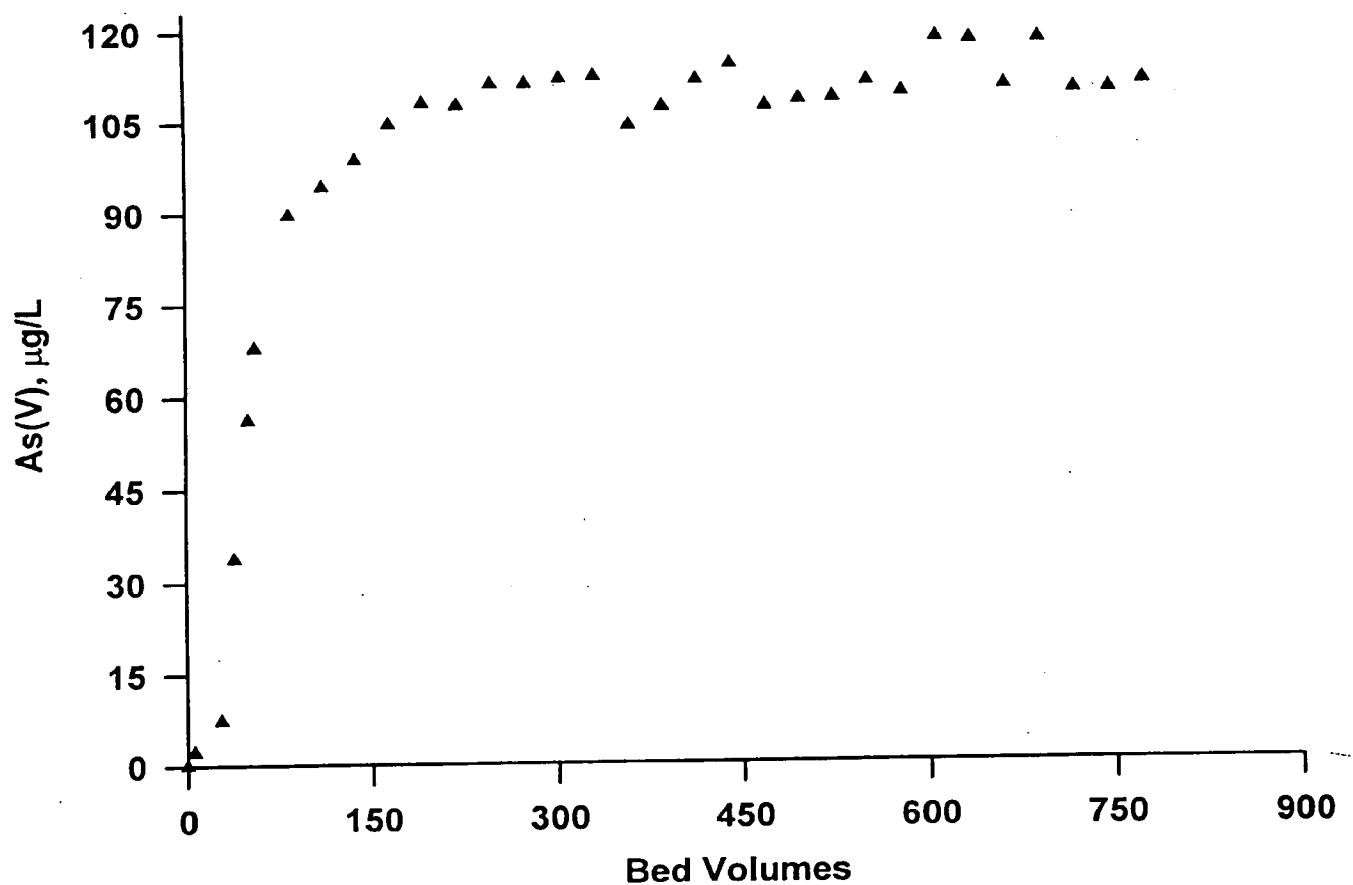


FIG. 2

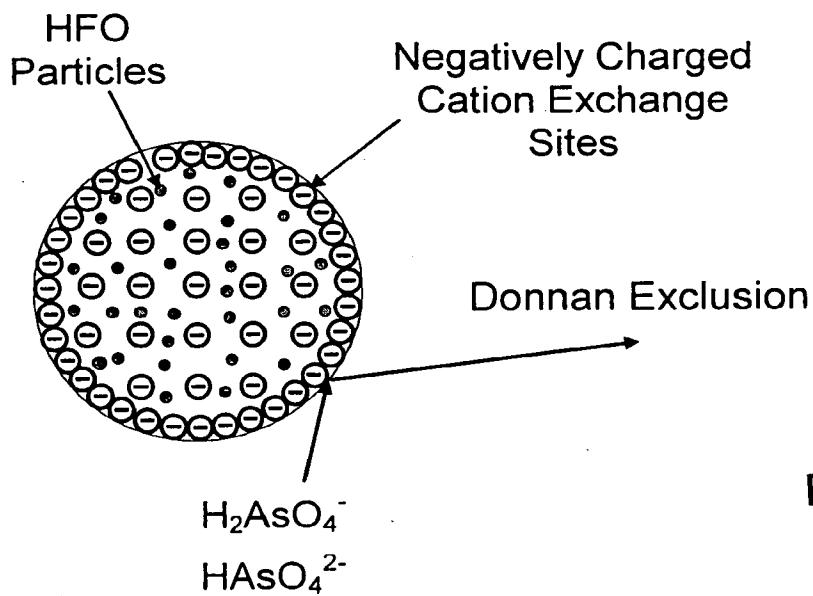


FIG. 3

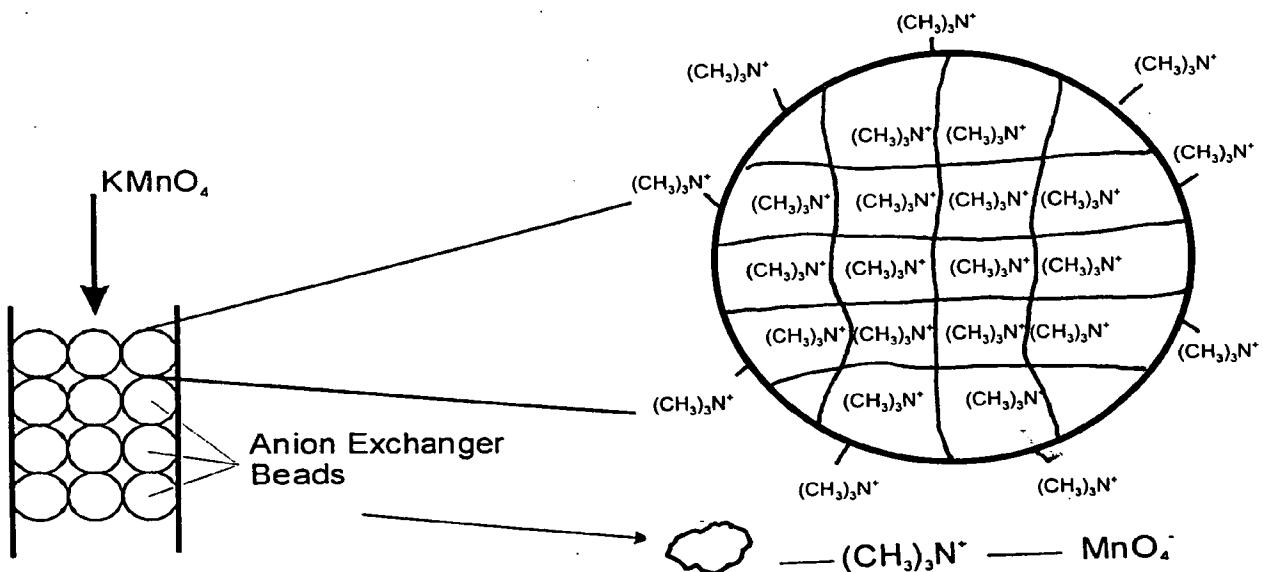


FIG. 4A

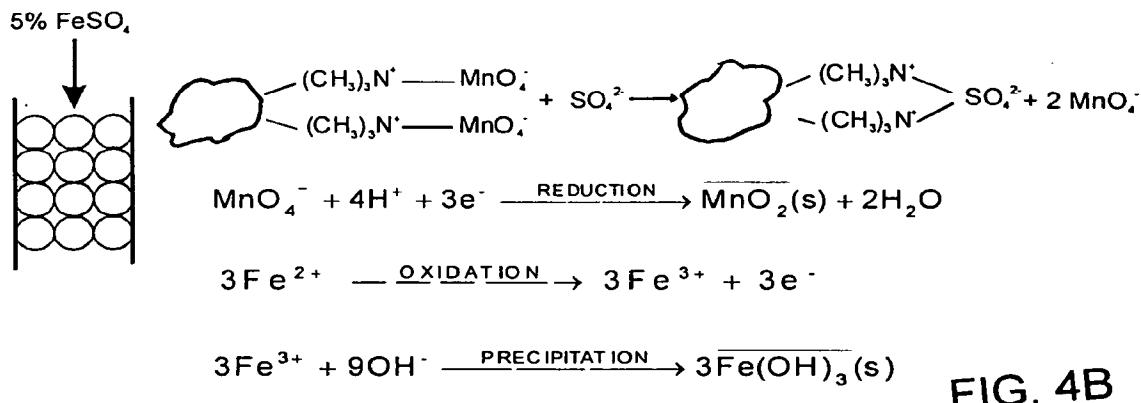


FIG. 4B

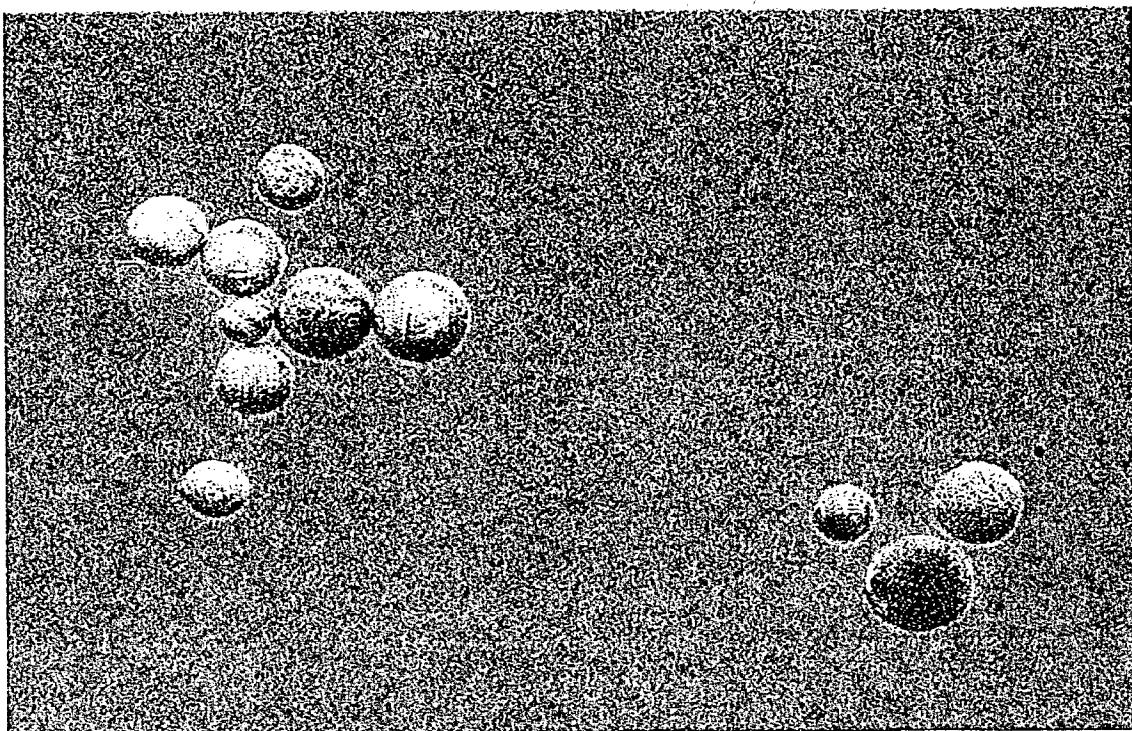


FIG. 5A

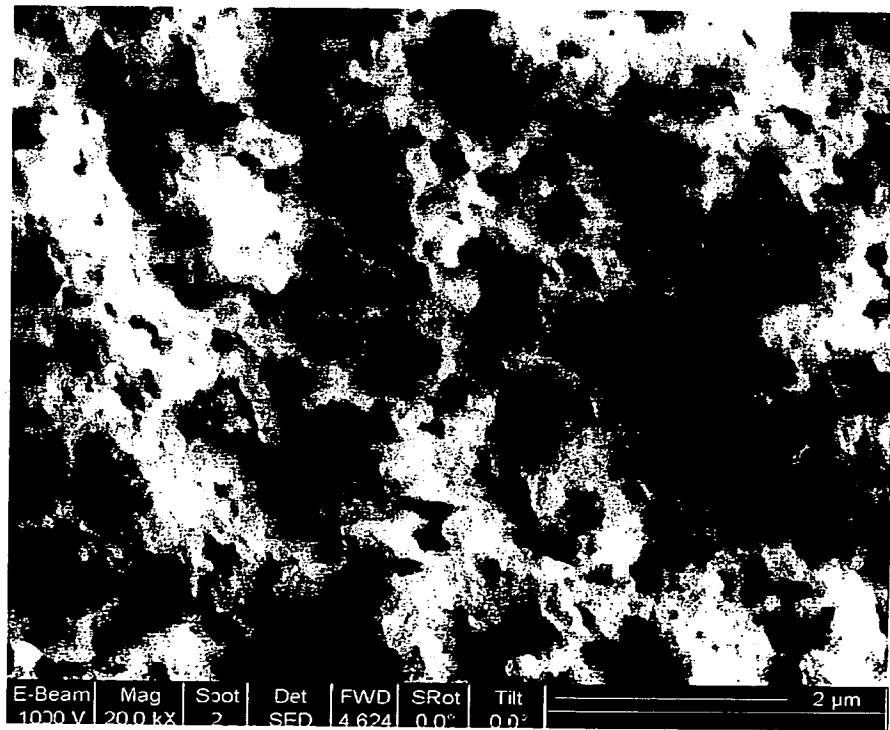
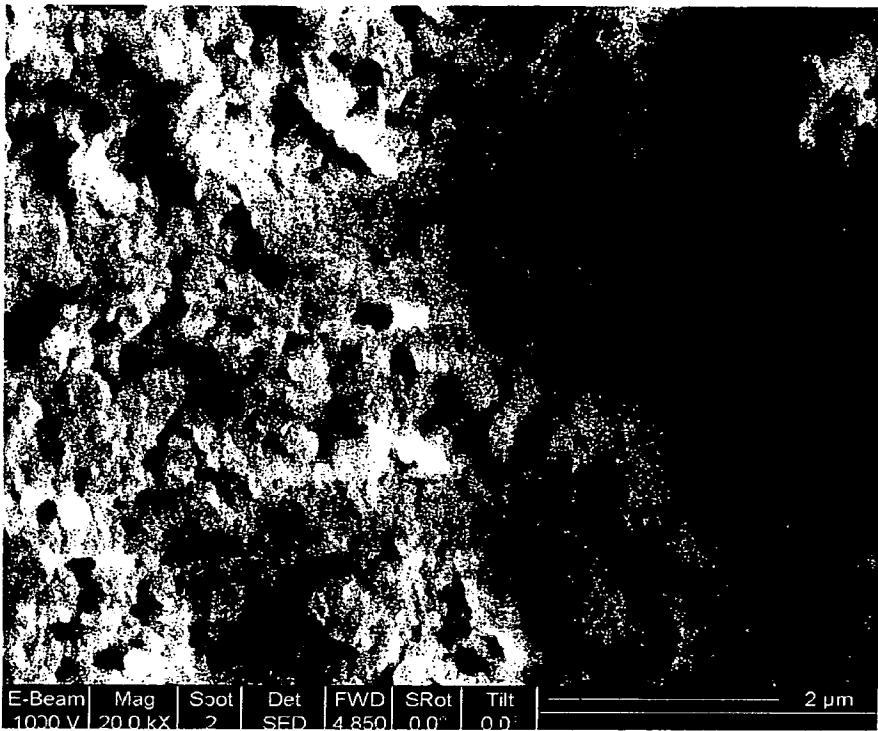


FIG. 5B



E-Beam	Mag	Soot	Det	FWD	SRot	Tilt		2 μm
1000 V	20.0 kX	2	SED	4.850	0.0°	0.0	-	

FIG. 5C

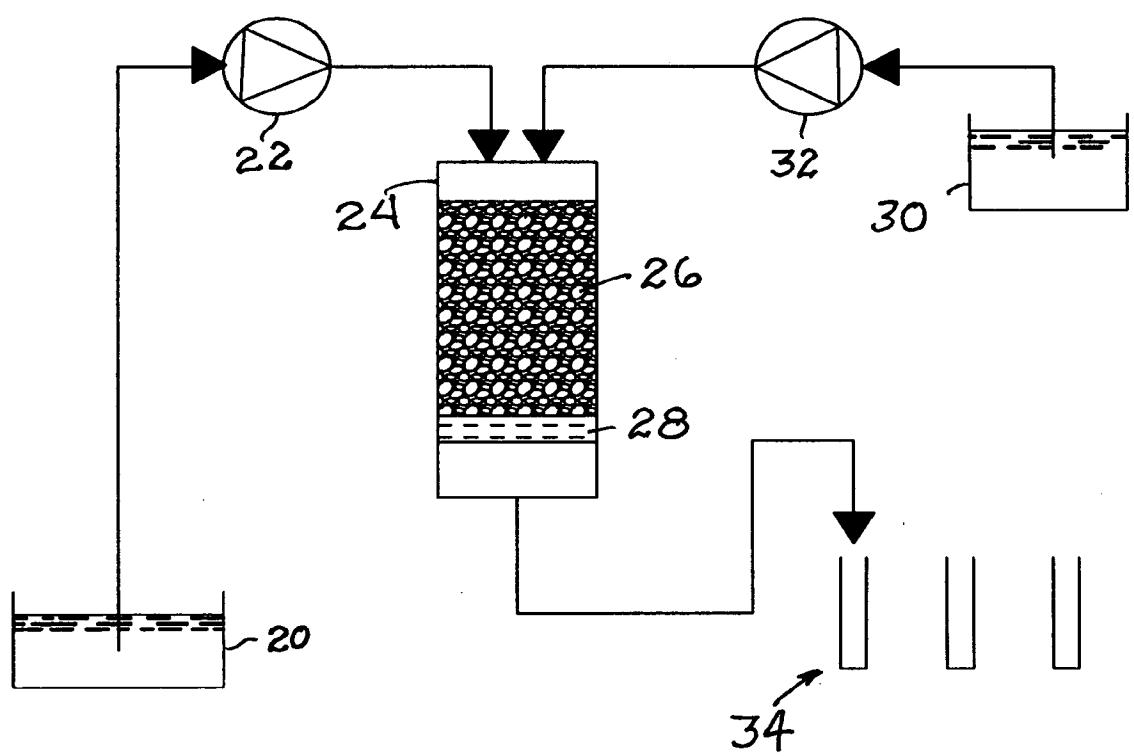


FIG. 6

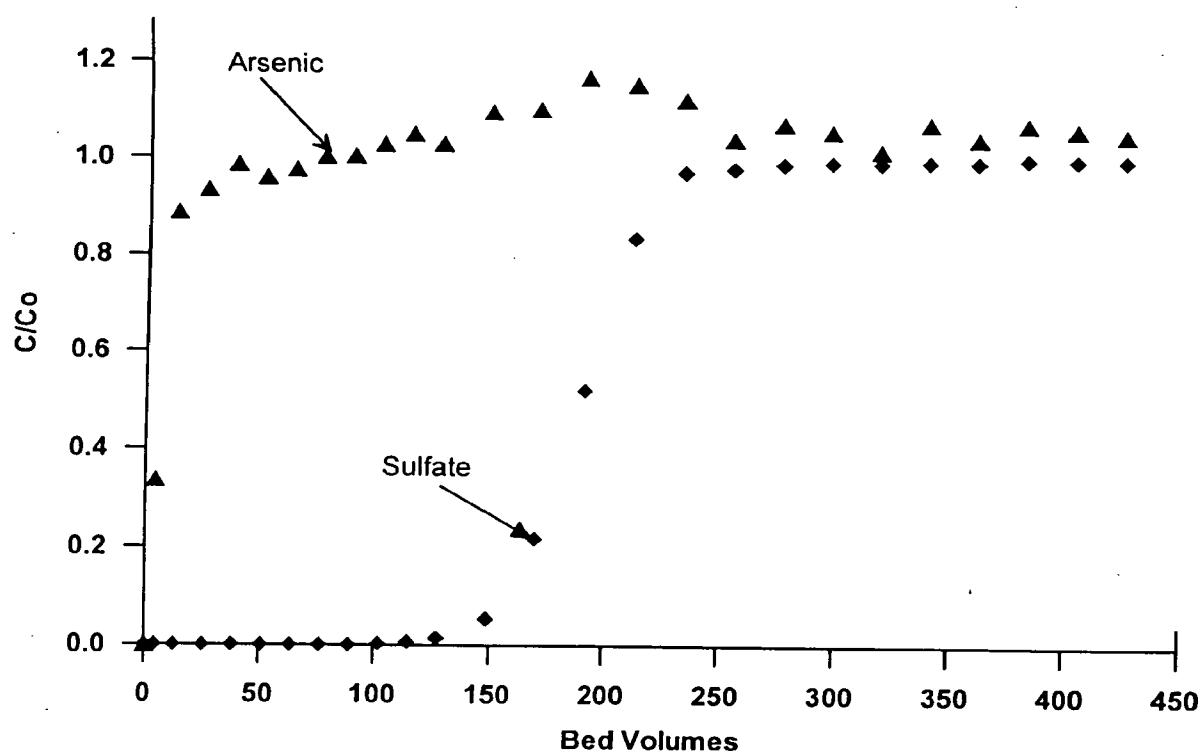


FIG. 7A

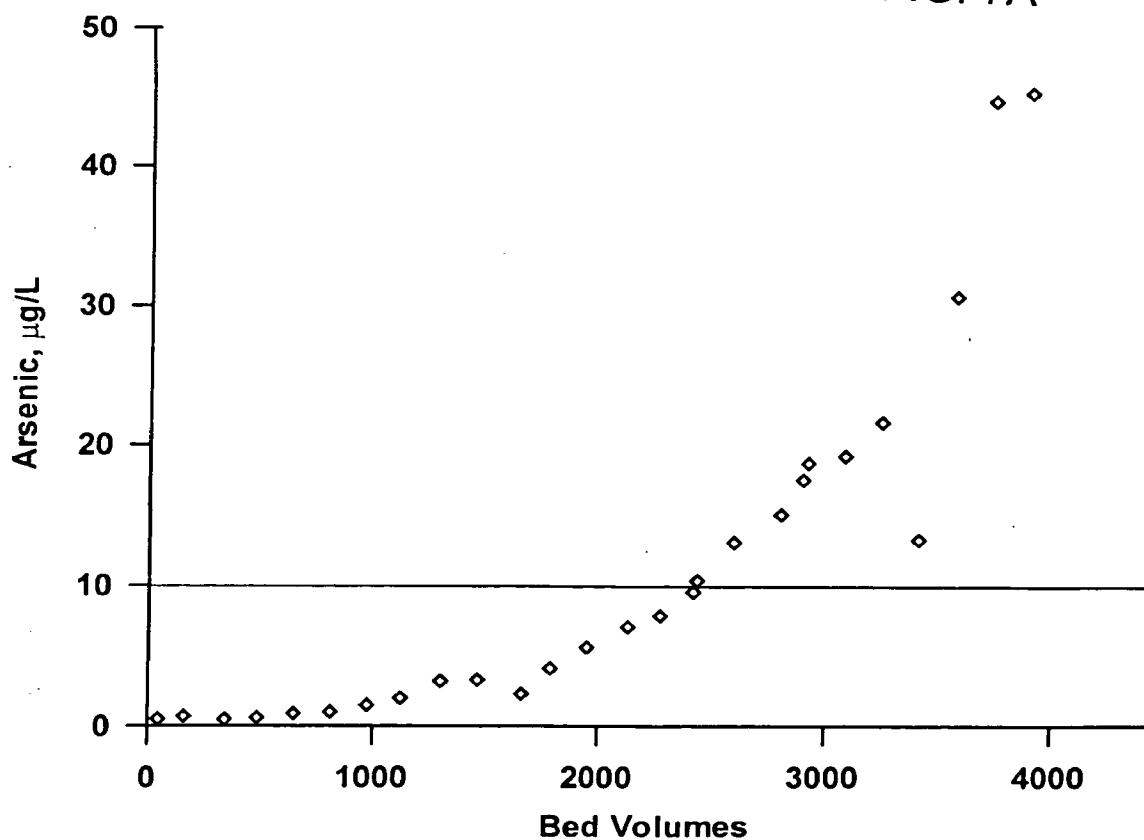


FIG. 7B

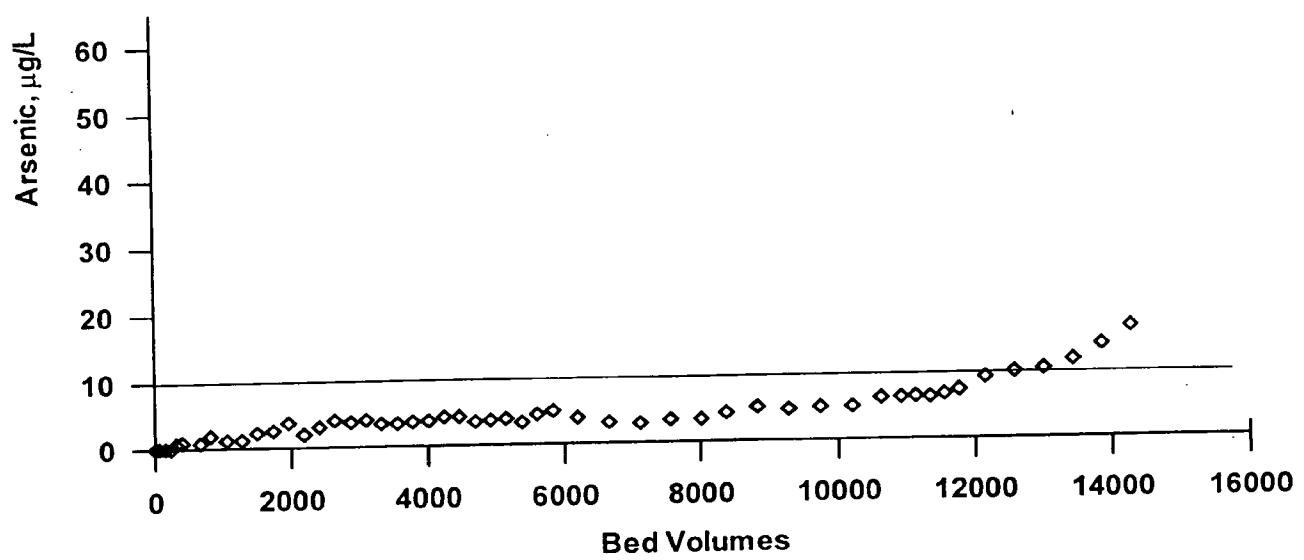


FIG. 7C

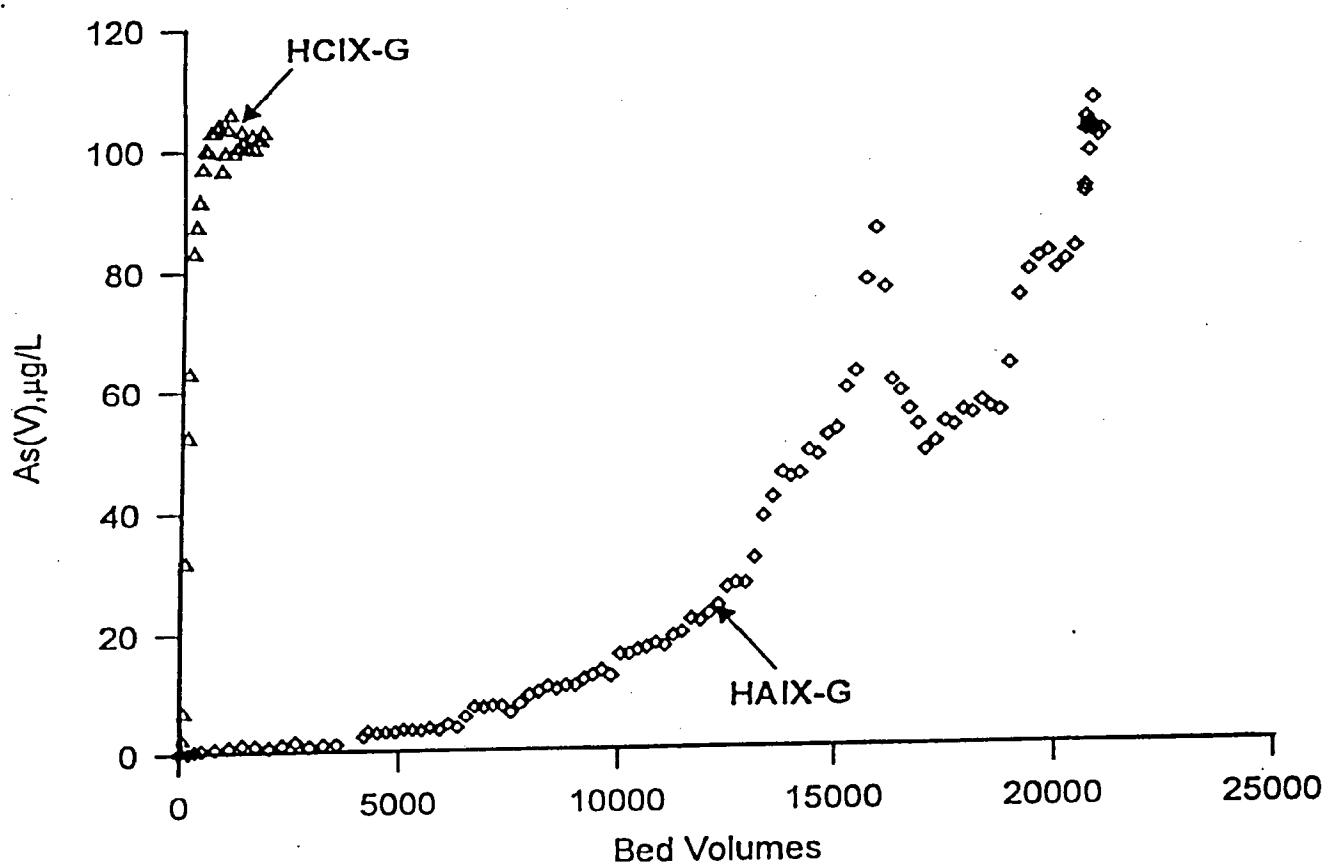


FIG. 8

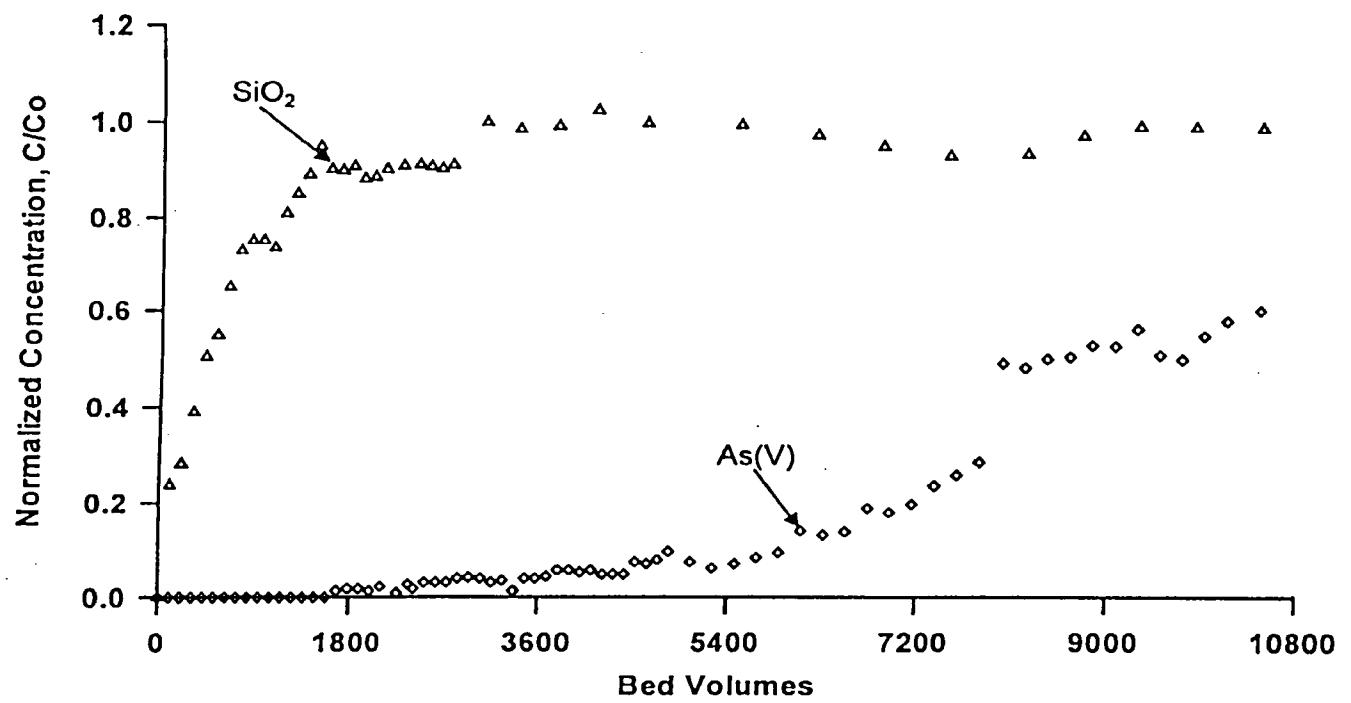


FIG. 9

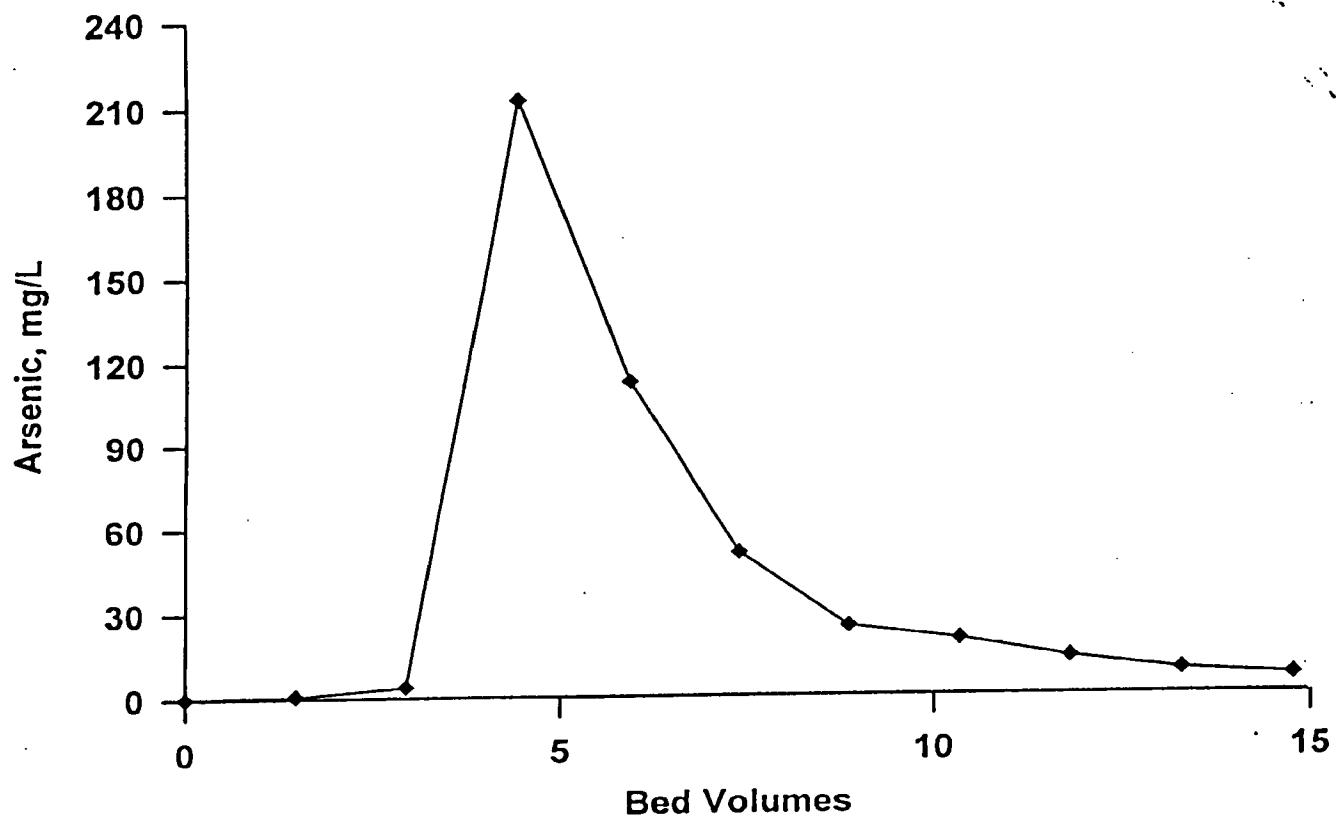


FIG. 10

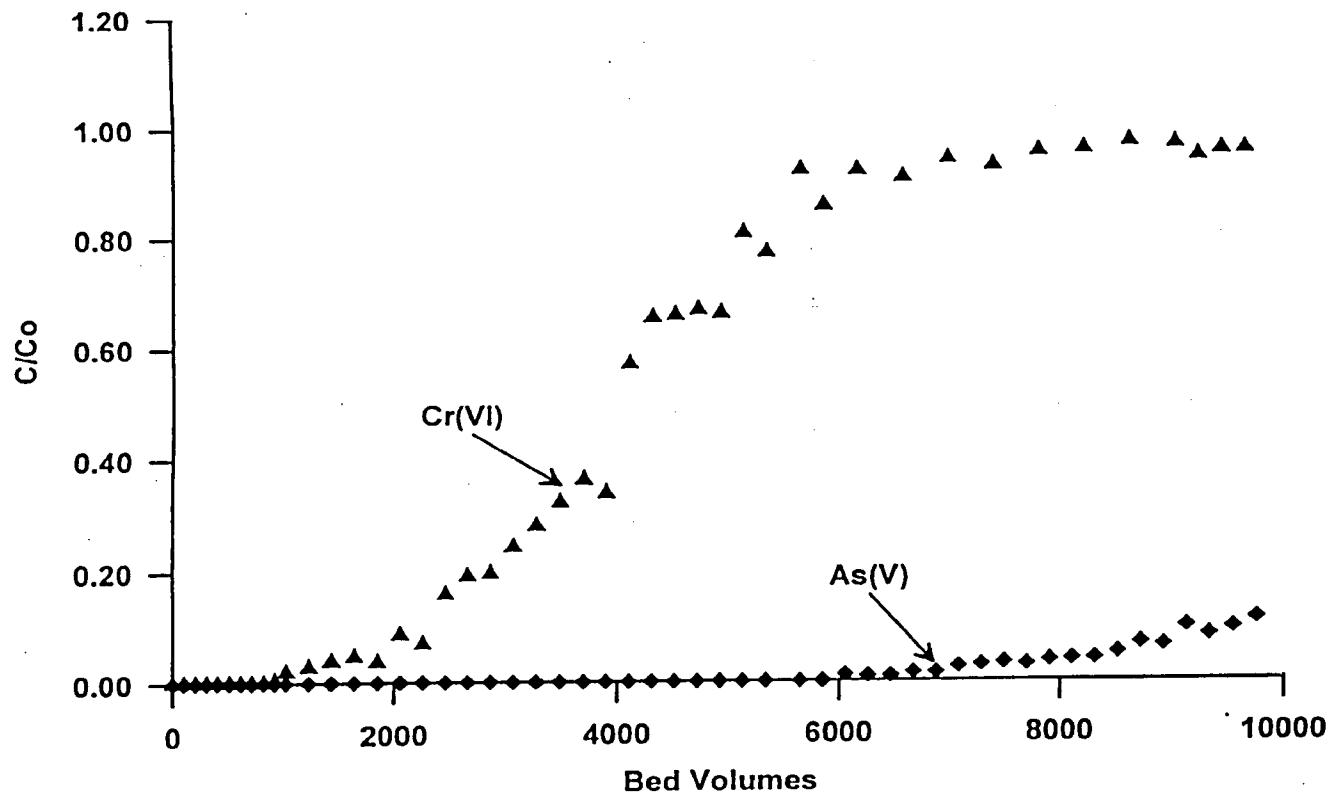


FIG. 11

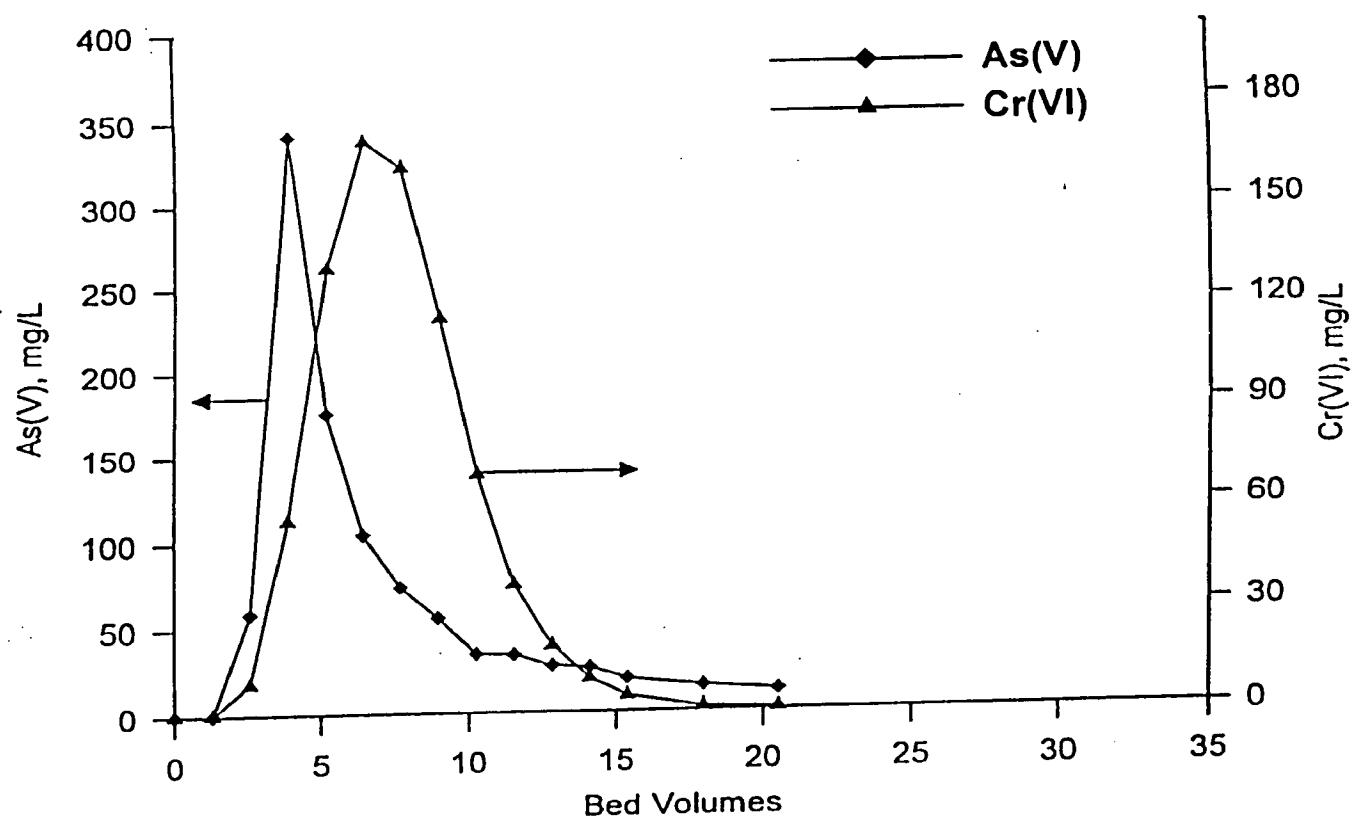


FIG. 12

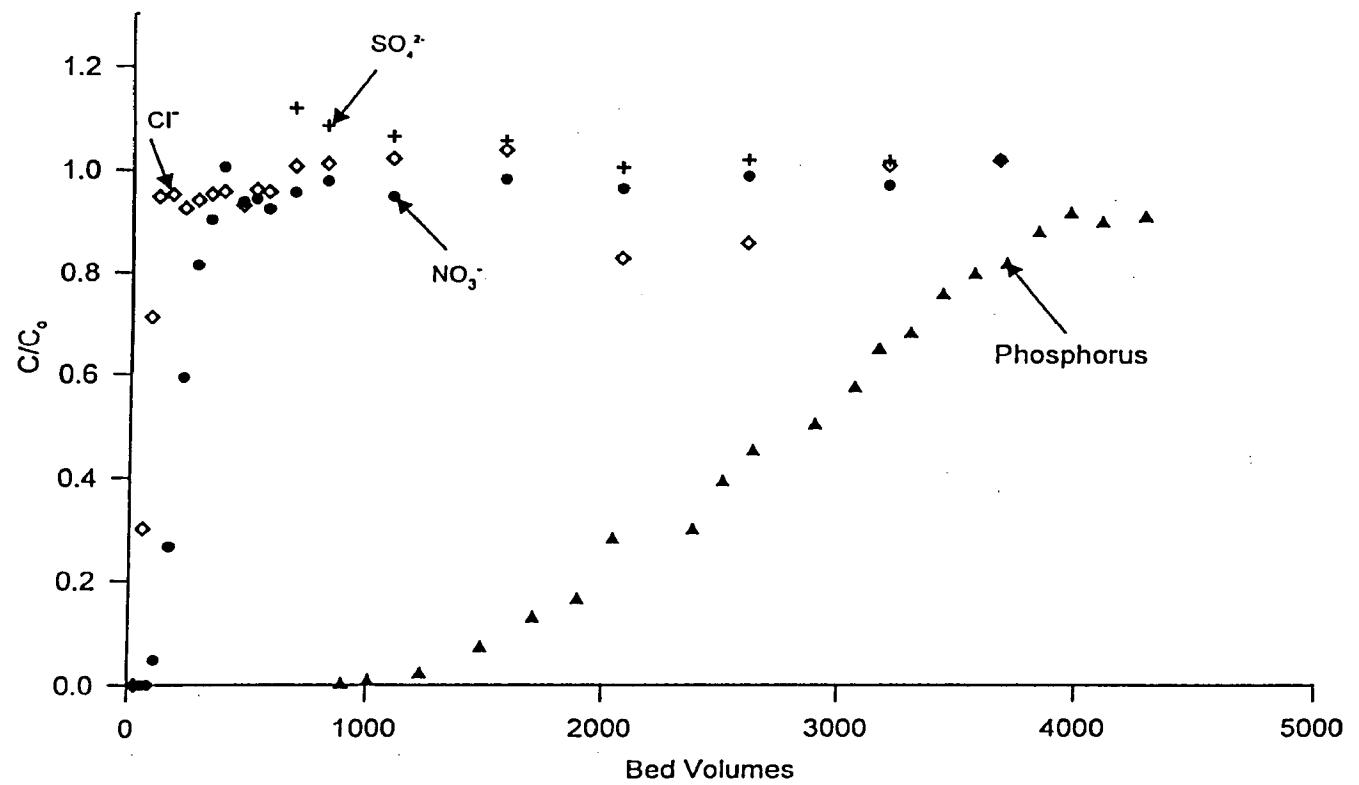


FIG. 13

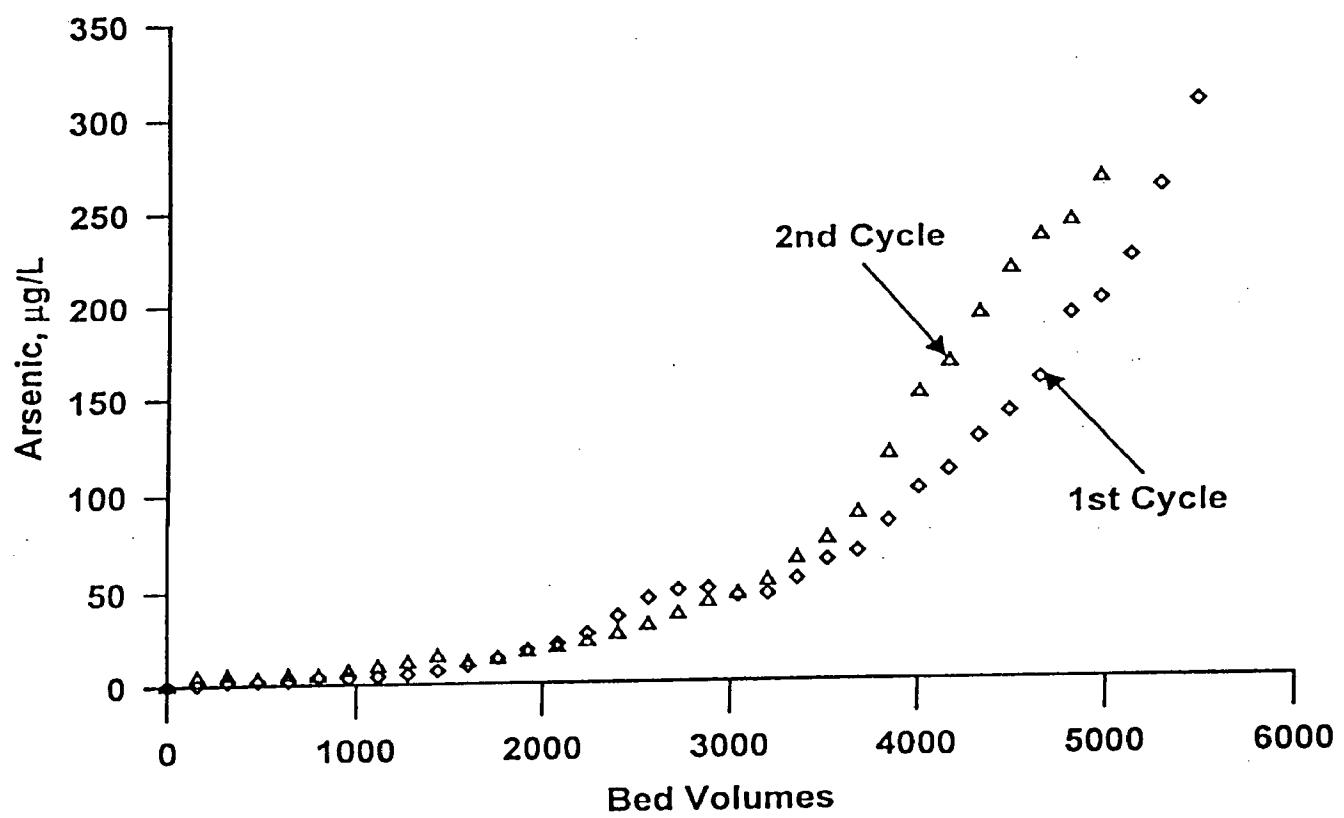


FIG. 14

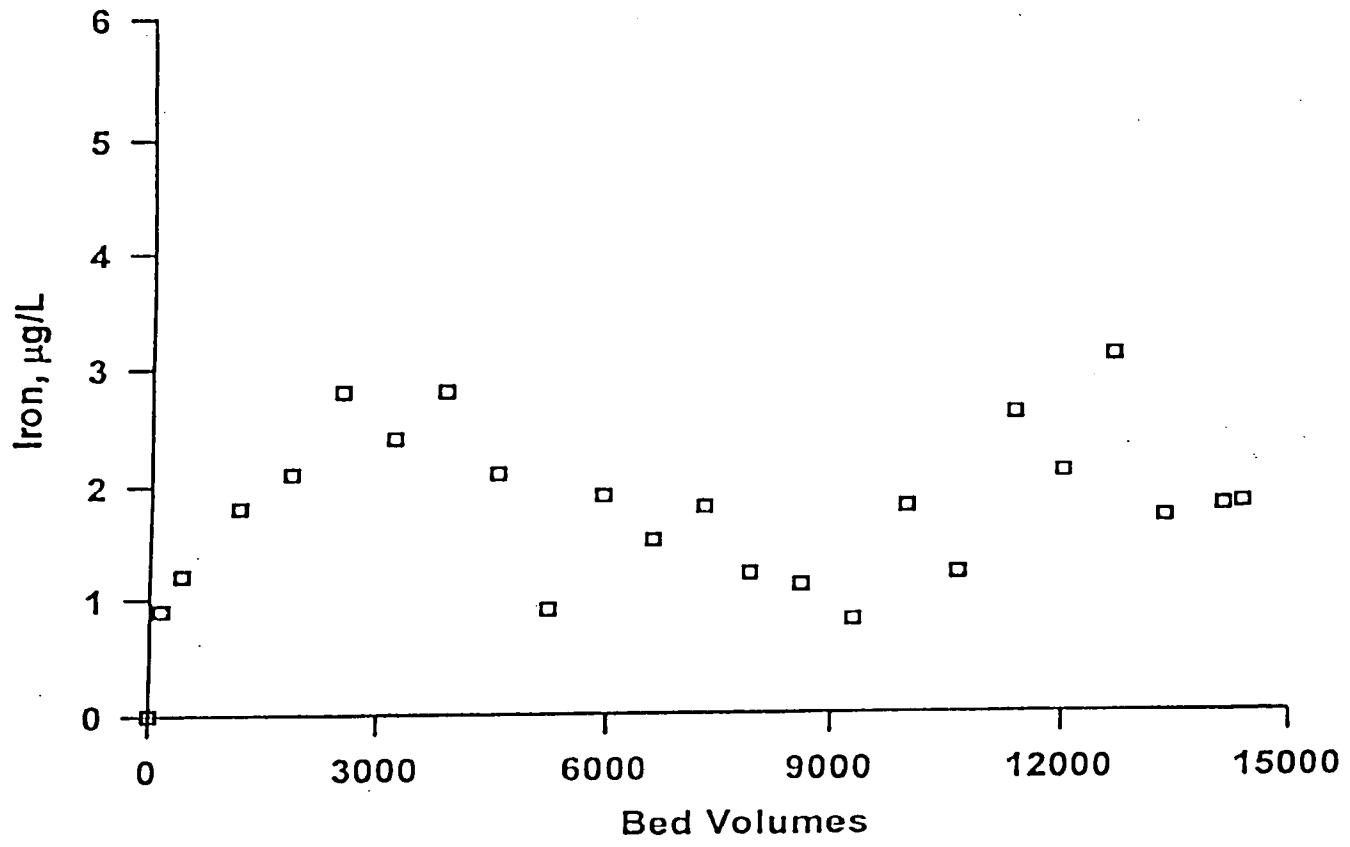


FIG. 15

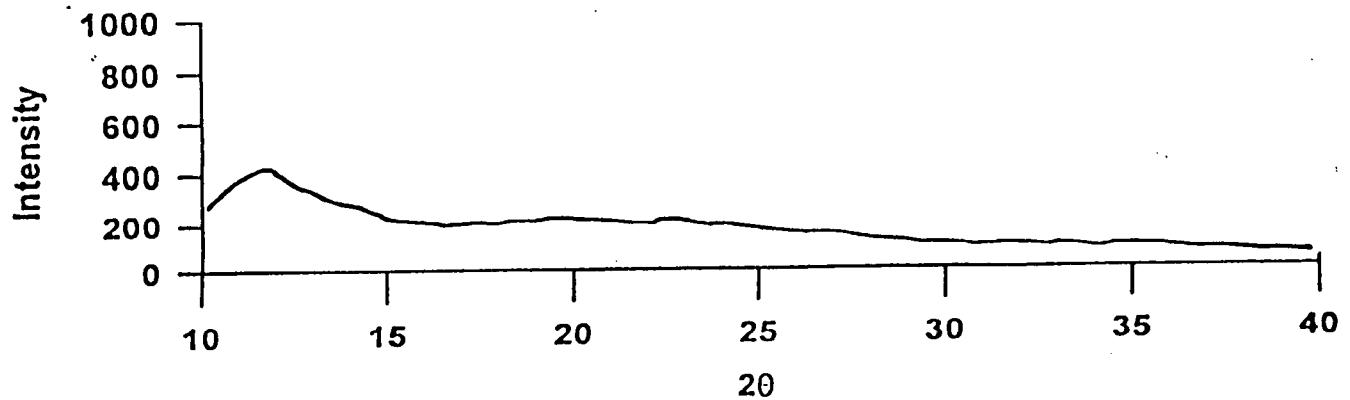


FIG. 16A

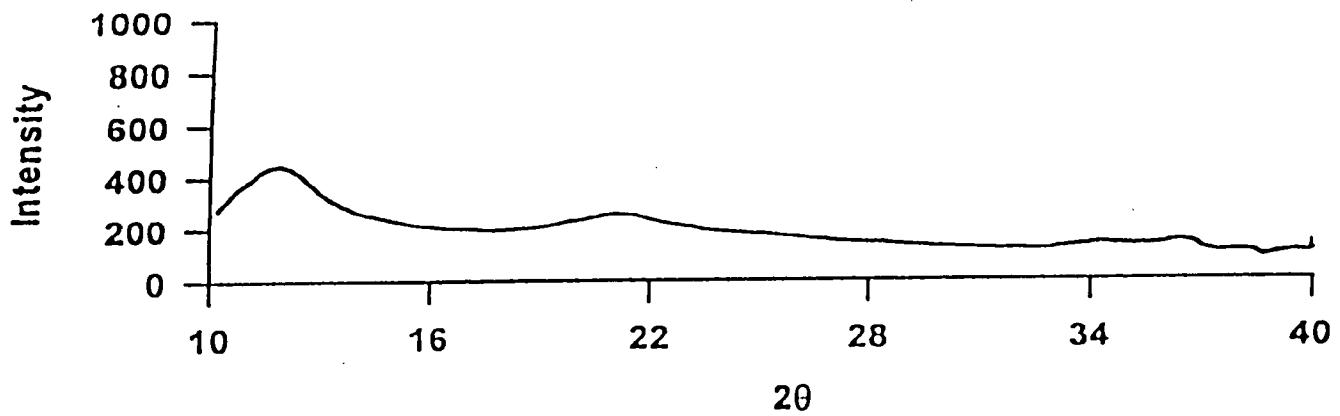


FIG. 16B

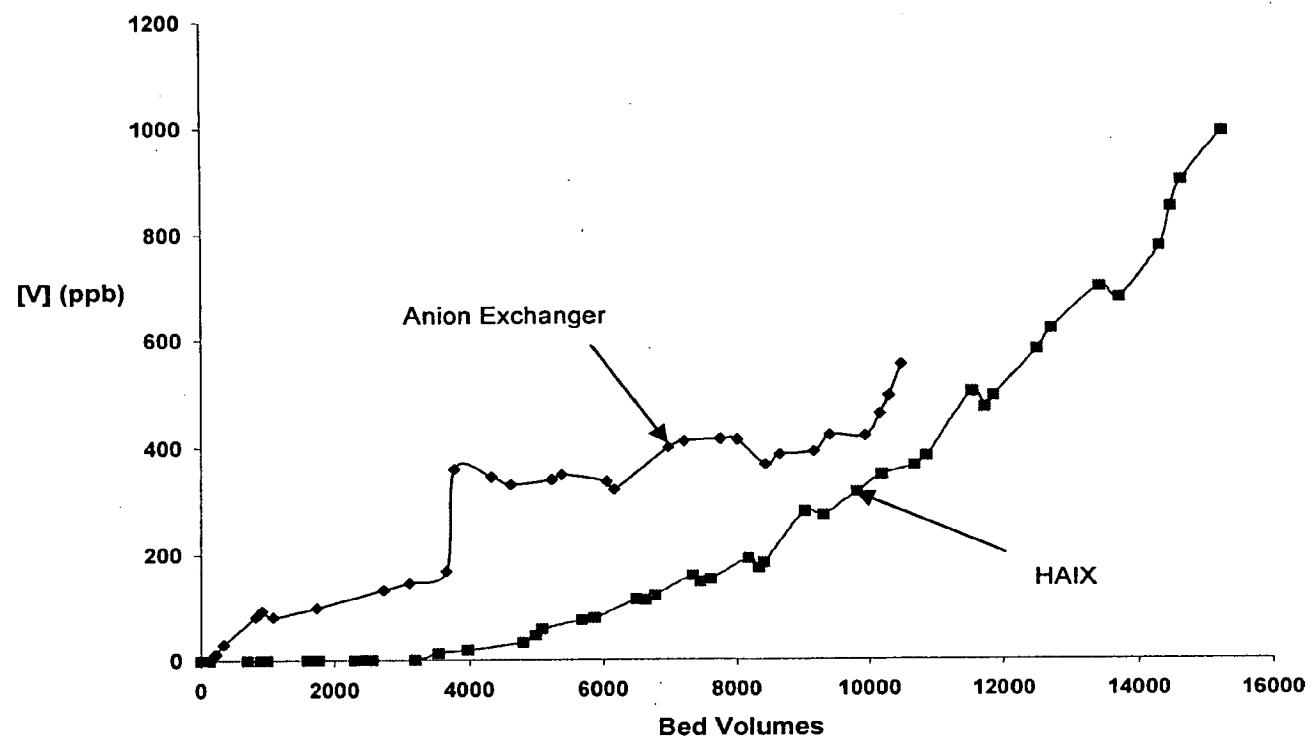


FIG. 17

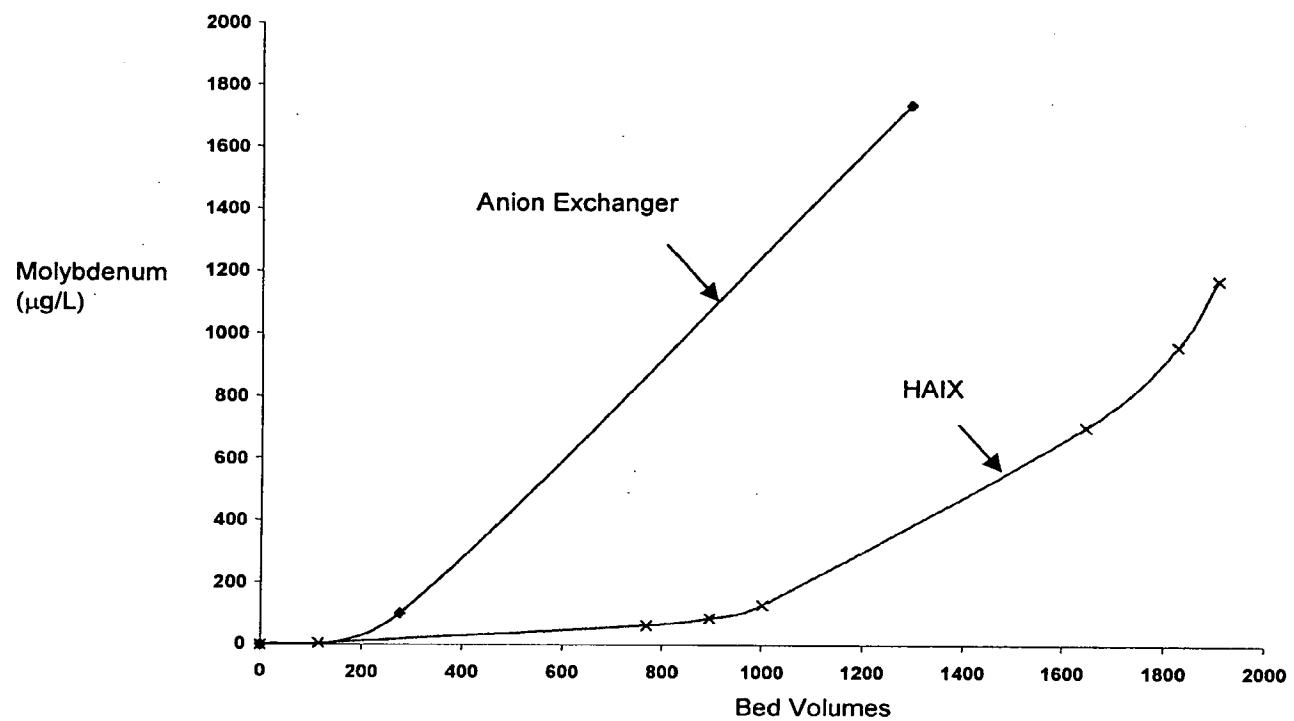


FIG. 18

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER: \_\_\_\_\_**

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

**DECLARATION FOR UTILITY OR  
DESIGN  
PATENT APPLICATION  
(37 CFR 1.63)**

Declaration Submitted With Initial Filing

**OR**

Declaration Submitted after Initial Filing (surcharge (37 CFR 1.16 (e)) required)

Attorney Docket Number	SEN3USA
First Named Inventor	Arup K. SenGupta et al <i>COMPLETE IF KNOWN</i>
Application Number	
Filing Date	
Art Unit	
Examiner Name	

**I hereby declare that:**

Each inventor's residence, mailing address, and citizenship are as stated below next to their name.

I believe the inventor(s) named below to be the original and first inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD OF MANUFACTURE AND USE OF HYBRID ANION EXCHANGER FOR SELECTIVE REMOVAL OF CONTAMINATING LIGANDS FROM FLUIDS

*(Title of the Invention)*

the specification of which

 is attached hereto**OR** was filed on (MM/DD/YYYY)  as United States Application Number or PCT InternationalApplication Number  and was amended on (MM/DD/YYYY)  (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or plant breeder's rights certificate(s), or any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? Yes	Certified Copy Attached? No
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

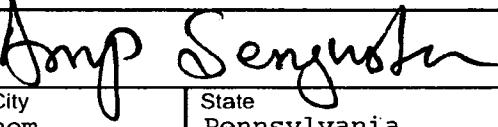
 Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

[Page 1 of 2]

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 21 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450; Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

**DECLARATION — Utility or Design Patent Application**

Direct all correspondence to: <input checked="" type="checkbox"/> Customer Number: 00270      OR <input type="checkbox"/> Correspondence address below			
Name			
Address			
City		State	
Country		Telephone	Fax
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.			
NAME OF SOLE OR FIRST INVENTOR:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any]) Arup K.		Family Name or Surname SenGupta	
Inventor's Signature 		Date Aug 21, 2004	
Residence: City Bethlehem	State Pennsylvania	Country U.S.	Citizenship U.S.
Mailing Address 3286. Marchant Drive.			
City Bethlehem	State Pennsylvania	ZIP 18017	Country U.S.
NAME OF SECOND INVENTOR:		<input type="checkbox"/> A petition has been filed for this unsigned inventor	
Given Name (first and middle [if any]) Luis H.		Family Name or Surname Cumbal	
Inventor's Signature 		Date 8/17/04	
Residence: City Quito	State	Country Ecuador	Citizenship Ecuador
Mailing Address Avenida Cardenal de la Torre S12-74 Ciudadela Primero de Mayo (El Calzado)			
City Quito	State	ZIP	Country Ecuador
<input type="checkbox"/> Additional inventors or a legal representative are being named on the _____ supplemental sheet(s) PTO/SB/02A or 02LR attached hereto.			

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

**POWER OF ATTORNEY  
and  
CORRESPONDENCE ADDRESS  
INDICATION FORM**

<b>Application Number</b>	
<b>Filing Date</b>	
<b>First Named Inventor</b>	Arup K. SenGupta et al.
<b>Title</b>	METHOD OF MANUFACTURING AND USE.
<b>Art Unit</b>	
<b>Examiner Name</b>	
<b>Attorney Docket Number</b>	SEN3USA

I hereby appoint:

Practitioners associated with the Customer Number:

00270

OR

Practitioner(s) named below:

Name	Registration Number

as my/our attorney(s) or agent(s) to prosecute the application identified above, and to transact all business in the United States Patent and Trademark Office connected therewith.

Please recognize or change the correspondence address for the above-identified application to:

The address associated with the above-mentioned Customer Number:

OR

The address associated with Customer Number:

OR

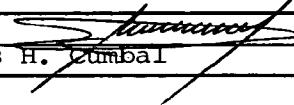
<input type="checkbox"/>	Firm or Individual Name	
Address		
Address		
City	State	Zip
Country		
Telephone	Fax	

I am the:

Applicant/Inventor.

Assignee of record of the entire interest. See 37 CFR 3.71.  
*Statement under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96)*

**SIGNATURE of Applicant or Assignee of Record**

Signature		Date	8/17/04
Name	Luis H. Cumbal	Telephone	
Title and Company			

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more than one signature is required, see below.

\*Total of 2 forms are submitted.

This collection of information is required by 37 CFR 1.31 and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

**POWER OF ATTORNEY  
and  
CORRESPONDENCE ADDRESS  
INDICATION FORM**

<b>Application Number</b>	
<b>Filing Date</b>	
<b>First Named Inventor</b>	Arup K. SenGupta et al.
<b>Title</b>	METHOD OF MANUFACTURE AND
<b>Art Unit</b>	
<b>Examiner Name</b>	
<b>Attorney Docket Number</b>	SEN3USA

USE..

I hereby appoint:

Practitioners associated with the Customer Number:

00270

OR

Practitioner(s) named below:

Name	Registration Number

as my/our attorney(s) or agent(s) to prosecute the application identified above, and to transact all business in the United States Patent and Trademark Office connected therewith.

Please recognize or change the correspondence address for the above-identified application to:

The address associated with the above-mentioned Customer Number:

OR

The address associated with Customer Number:

OR

<input type="checkbox"/>	Firm or Individual Name			
Address				
Address				
City		State	Zip	
Country				
Telephone		Fax		

I am the:

Applicant/Inventor.  
 Assignee of record of the entire interest. See 37 CFR 3.71.  
Statement under 37 CFR 3.73(b) is enclosed. (Form PTO/SB/96)

**SIGNATURE of Applicant or Assignee of Record**

Signature		Date	Aug 21, 2009
Name	Arup K. SenGupta	Telephone	
Title and Company			

NOTE: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required. Submit multiple forms if more than one signature is required, see below.

\*Total of 2 forms are submitted.

This collection of information is required by 37 CFR 1.31 and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

## **APPLICATION DATA SHEET**

### **Application Information**

Application Type:: Regular  
Subject Matter:: Utility  
Suggested Classification::  
Suggested Group Art Unit::  
CD-ROM or CD-R?:: None  
Number of CD disks::  
Number of Copies of CDs::  
Sequence Submission?::  
Computer Readable Form (CRF)?::  
Number of Copies of CRF::  
Title:: METHOD OF MANUFACTURE AND  
USE OF HYBRID ANION  
EXCHANGER FOR SELECTIVE  
REMOVAL OF CONTAMINATING  
LIGANDS FROM FLUIDS  
Attorney Docket Number:: SEN3USA  
Request for Early Publication:: No  
Request for non-Publication:: No  
Suggested Drawing Figure::  
Total Drawing Sheets:: 19  
Small Entity:: Yes  
Latin name::  
Variety denomination name::  
Petition Included?:: No  
Petition Type::  
Licensed US Govt. Agency::  
Contract or Grant Numbers::  
Secrecy Order in Parent Application:: No

## **Applicant Information**

Applicant Authority Type::	Inventor
Primary Citizenship Country::	US
Status::	Full Capacity
Given Name::	Arup
Middle Name::	K.
Family Name::	SenGupta
Name Suffix::	
City of Residence::	Bethlehem
State or Province of Residence::	PA
Country of Residence::	US
Street of Mailing Address::	3286 Marchant Dr.
City of Mailing Address::	Bethlehem
State or Province of Mailing Address::	PA
Country of Mailing Address::	US
Postal or Zip Code of Mailing Address::	18017

## **Applicant Information**

Applicant Authority Type::	Inventor
Primary Citizenship Country::	Ecuador
Status::	Full Capacity
Given Name::	Luis
Middle Name::	H.
Family Name::	Cumbal
Name Suffix::	
City of Residence::	Quito
State or Province of Residence::	Ciudadela Primero de Mayo (El Cazado)
Country of Residence::	Ecuador
Street of Mailing Address::	Avenida Cardenal de la Torre S12-74
City of Mailing Address::	Quito
State or Province of Mailing Address::	Ciudadela Primero de Mayo (El Cazado)
Country of Mailing Address::	Ecuador
Postal or Zip Code of Mailing Address::	

**Correspondence Information**

Correspondence Customer Number:: 00270  
Name:: Howson and Howson  
Street of Mailing Address:: Spring House Corporate Center, Box 457  
City of Mailing Address:: Spring House  
State or Province of Mailing Address:: Pennsylvania  
Country of Mailing Address:: US  
Postal or Zip Code of Mailing Address:: 19477  
Telephone:: 215-540-9200  
Telefacsimile:: 215-540-5818  
E-Mail Address:: gasmith@howsonandhowson.com

**Representative Information**

Representative Customer Number::	00270	
----------------------------------	-------	--

**Domestic Priority Information**

Application::	Continuity Type::	Parent Application::	Parent Filing Date::
This Application	An application claiming the benefit under 35USC119(e)	60/538,131	01/21/2004

**Foreign Priority Information**

Country::	Application Number::	Filing Date::	Priority Claimed::

### **Assignee Information**

Assignee Name:: Arup K. SenGupta  
Street of Mailing Address:: 3286 Marchant Drive  
City of Mailing Address:: Bethlehem  
State or Province of Mailing Address:: PA  
Country of Mailing Address:: US  
Postal or Zip Code of Mailing Address:: 18017